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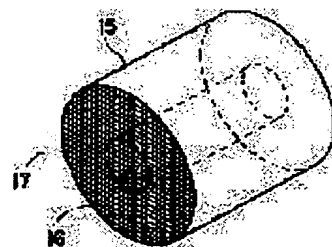
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(54) ADSORPTIVE/CATALYTIC ELEMENT FOR EXHAUST GAS PURIFICATION, ADSORPTIVE ELEMENT, EXHAUST GAS PURIFICATION SYSTEM AND EXHAUST GAS PURIFICATION

(57)Abstract:

PURPOSE: To make it possible to purify an organic substance contained in an exhaust gas efficiently by separating a hydrocarbon adsorptive layer from a catalytic layer having three-dimensional function or oxidation function in a direction at right angles with a gas flowing direction and in a certain cross-section, and causing these layers to be borne on a honeycomb structure partitioned by a diaphragm and with through holes arranged parallel to a gas flowing direction.

CONSTITUTION: An exhaust gas purification adsorptive/catalytic element consists of an adsorptive layer 17 with a hydrocarbon adsorptive function and a catalytic layer 16 with three-dimensional function or oxidation function borne on a honeycomb structure 15 partitioned by a diaphragm and with through holes arranged substantially parallel to a gas flowing direction. The adsorptive layer 17 and the catalytic layer 16 are borne by a structure, being separated in a certain cross-section, in a direction at right angles with the gas flowing direction. Consequently, it is



possible to purify a harmful substance contained in an exhaust gas blown out of an internal combustion engine, especially, HC generated in large quantities at the time of cold start.

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CLAIMS

[Claim(s)]

[Claim 1] The adsorption and the catalyst object for emission gas purification which are the adsorption and a catalyst object for emission gas purification with which it comes to support the catalyst bed which has the adsorption layer, the 3 yuan engine performance, or the oxidation engine performance have hydrocarbon adsorption capacity on the honeycomb structure object which has the through tube of parallel a large number substantially in the gas flow direction divided by the septum, and is characterize by for an adsorption layer and a catalyst bed to dissociate and to be support it with a certain cross section in said gas flow direction and direction of a right angle

[Claim 2] The adsorption and the catalyst object for emission gas purification according to claim 1 whose cross section of the part with which the catalyst bed was supported is 5 - 80% of the cross section of a honeycomb structure object.

[Claim 3] The adsorption and the catalyst object for emission gas purification according to claim 1 whose heat capacity of the part with which the adsorption layer was supported is size from the heat capacity of the part with which the catalyst bed was supported.

[Claim 4] The adsorption and the catalyst object for emission gas purification according to claim 1 with the die length shorter than the die length to the gas flow direction of a part where the adsorption layer was supported to some [at least] gas flow directions where the catalyst bed was supported.

[Claim 5] The adsorption and the catalyst object for emission gas purification according to claim 1 some of [at least] whose numerical apertures with which the catalyst bed was supported are size from the numerical aperture of the part with which the adsorption layer was supported.

[Claim 6] The adsorption and the catalyst object for emission gas purification according to claim 1 to 5 with which covering support of the layer which a catalyst component is contained in an adsorption layer, or contains a catalyst component on the surface of an adsorption layer was carried out.

[Claim 7] The adsorption and the catalyst object for emission gas purification according to claim 1 to 6 with which an adsorption layer uses a zeolite as a principal component.

[Claim 8] The adsorption and the catalyst object for emission gas purification according to claim 7 whose Si/aluminum mole ratio of a zeolite is 40 or more.

[Claim 9] The adsorption and the catalyst object for emission gas purification according to claim 7 with which a kind of noble metals of Pt, Pd, and the Rh(s) are contained at least in a zeolite.

[Claim 10] The adsorption and the catalyst object for emission gas purification according to claim 7 with which at least one sort of ion of IB group element (Cu, Ag, Au) of a periodic table is contained in a zeolite.

[Claim 11] The adsorption and the catalyst object for emission gas purification according to claim 10 whose content of the ion of IB group element in a zeolite is 20% or more to aluminum atom in a zeolite.

[Claim 12] The adsorption and the catalyst object for emission gas purification according to claim 10 with which a kind of ion further chosen from the various ion of Mg, calcium, Sr, Ba, Y, La, Ti, Ce, Mn, Fe, Cr, nickel, and Zn was contained at least in the zeolite.

[Claim 13] The adsorption and the catalyst object for emission gas purification according to claim 1 to

12 with which a catalyst bed contains a kind of noble metals of Pt, Pd, and the Rh(s) at least.

[Claim 14] Adsorbent for emission gas purification characterized by forming the blow-by section to which it is the adsorbent for emission gas purification with which it comes to support the adsorption layer which has hydrocarbon adsorption capacity, and exhaust gas blows these some honeycomb structure objects on the honeycomb structure object which has the through tube of parallel a large number divided by the septum.

[Claim 15] Adsorbent for emission gas purification according to claim 14 by which the blow-by section was formed in the through tube of a honeycomb structure object, and parallel.

[Claim 16] Predetermined adsorbent for emission gas purification according to claim 14 in which the blow-by section made it incline the degree of angle to the through tube of a honeycomb structure object, and it was formed.

[Claim 17] Adsorbent for emission gas purification according to claim 14 to 16 by which covering support of the layer which a catalyst component is contained in an adsorption layer, or contains a catalyst component on the surface of an adsorption layer was carried out.

[Claim 18] Adsorbent for emission gas purification according to claim 14 to 17 to which an adsorption layer uses a zeolite as a principal component.

[Claim 19] Adsorbent for emission gas purification according to claim 18 whose Si/aluminum mole ratio of a zeolite is 40 or more.

[Claim 20] Adsorbent for emission gas purification according to claim 18 by which a kind of noble metals of Pt, Pd, and the Rh(s) are contained at least in a zeolite.

[Claim 21] Adsorbent for emission gas purification according to claim 18 by which at least one sort of ion of IB group element (Cu, Ag, Au) of a periodic table is contained in a zeolite.

[Claim 22] Adsorbent for emission gas purification according to claim 21 whose content of the ion of IB group element in a zeolite is 20% or more to aluminum atom in a zeolite.

[Claim 23] Adsorbent for emission gas purification according to claim 21 by which a kind of ion further chosen from the various ion of Mg, calcium, Sr, Ba, Y, La, Ti, Ce, Mn, Fe, Cr, nickel, and Zn was contained at least in the zeolite.

[Claim 24] The emission-gas-purification system characterized by installing at least one adsorption and a catalyst object according to claim 1 to 13 in an exhaust pipe, and coming further to install the catalyst object with which it comes to support a catalyst bed on a honeycomb structure object at the exhaust gas flow direction downstream of this adsorption and catalyst object.

[Claim 25] Furthermore, the emission-gas-purification system according to claim 24 which installed the catalyst object with which it comes to support a catalyst bed on the honeycomb structure object also at the improvement style side in the method of exhaust gas flowing of adsorption and a catalyst object.

[Claim 26] Furthermore, the emission-gas-purification system according to claim 24 which installed the electric energization heating type heater between adsorption and the catalyst object, and the catalyst object.

[Claim 27] Furthermore, the emission-gas-purification system of the catalyst object installed between adsorption and a catalyst object, and a catalyst object and/or in the improvement style side in the method of exhaust gas flowing of adsorption and a catalyst object according to claim 25 which installed the electric energization heating type heater in the upstream further.

[Claim 28] The emission-gas-purification system according to claim 24 to 27 by which it was made for the amount of emission of the part with which channeling of the exhaust gas was carried out and the catalyst bed of adsorption and a catalyst object was supported to become larger than the amount of emission of the part with which the adsorption layer was supported.

[Claim 29] Furthermore, the emission-gas-purification system according to claim 24 to 28 which installed at least one adsorbent according to claim 14 to 23 in the improvement style side in the method of exhaust gas flowing rather than the catalyst object installed in the exhaust gas flow direction downstream of adsorption and a catalyst object.

[Claim 30] The emission-gas-purification system characterized by installing at least one adsorbent according to claim 14 to 23 in an exhaust pipe, and coming further to install the catalyst object with

which it comes to support a catalyst bed on a honeycomb structure object at the exhaust gas flow direction downstream of this adsorbent.

[Claim 31] Furthermore, the emission-gas-purification system according to claim 30 which installed the catalyst object with which it comes to support a catalyst bed on the honeycomb structure object also at the improvement style side in the method of exhaust gas flowing of adsorbent.

[Claim 32] Furthermore, the emission-gas-purification system according to claim 30 which installed the electric energization heating type heater between adsorbent and a catalyst object.

[Claim 33] Furthermore, the emission-gas-purification system of the catalyst object installed between adsorbent and a catalyst object and/or in the improvement style side in the method of exhaust gas flowing of adsorbent according to claim 31 which installed the electric energization heating type heater in the upstream further.

[Claim 34] The emission-gas-purification system according to claim 30 to 33 carry out channeling of the exhaust gas, a part of emission blows, and it was made to pass the section.

[Claim 35] An emission-gas-purification system according to claim 24 to 34 is used. In the process in which the adsorption layer of adsorption and a catalyst object, and/or adsorbent is adsorbed, and the hydrocarbon in the exhaust gas which occurs at the time of an internal combustion engine's cold start etc. is desorbed from this adsorption layer in connection with the temperature rise by the exhaust gas of this adsorption layer The emission-gas-purification approach which considers as the exhaust gas presentation of hyperoxia and is characterized by making the hydrocarbon from which it was desorbed burn in the catalyst bed of adsorption and a catalyst object, and/or a catalyst object by adding a oxidizing gas in a certain fixed period exhaust gas, or performing accommodation with a combustion air and fuel quantity.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the emission-gas-purification system and the emission-gas-purification approach of purifying effectively the harmful matter in exhaust gas, especially the hydrocarbon (HC) generated so much at the time of a cold start.

[0002]

[Description of the Prior Art] In the FTP trial (LA-4 mode) corresponding to U.S. exhaust gas toughening of regulations, 7 - 80 percent of the total amount of HC emission is emitted within 140 (less than 1 crest acceleration) seconds at the time of the cold start after an engine crank. However, since the conventional three way component catalyst requires most time amount in the meantime until it reaches operative temperature, a great portion of HC will be emitted while not having been purified by it.

[0003] In order to solve this problem, the technique which arranges the catalyst (it is called "EHC" below Electrically-Heated Catalyst;) of an electric energization heating method and the adsorption material which uses a zeolite as a principal component all over an exhaust gas pipe way is proposed. For example, although three elements of sequence of EHC, adsorbent, and the Main catalyst are arbitrary, the catalytic converter for automobile exhaust purification arranged on the emission way at the serial is indicated by JP,5-31359,A. Moreover, SAE paper [0004] as which the bypass method which installs a bulb in the upstream of adsorption material is proposed as an approach of desorbing No.920847 from HC in the phase where the catalyst was fully activated

[Problem(s) to be Solved by the Invention] However, especially in JP,5-31359,A, the arrangement optimal for the emission reduction at the time of a cold start about the three above-mentioned elements is not indicated, and the consideration about stopping the injection power to EHC low etc. is not made, either. Moreover, SAE paper Although what adopted the bypass method like No.920874 acts suitably in respect of decontamination capacity, the dependability of the heat-resistant bulb in that a system becomes complicated and piping has become [many problems] scarce practically.

[0005] This invention is made in view of the trouble of the above conventional techniques, and the place made into the purpose is to offer the adsorption and the catalyst object for emission gas purification which can purify effectively the harmful matter in exhaust gas, especially HC generated so much at the time of a cold start, adsorbent, an emission-gas-purification system, and the emission-gas-purification approach, without requiring a complicated system like a bypass method.

[0006]

[Means for Solving the Problem] According to this invention, on the honeycomb structure object which has the through tube of parallel a large number substantially in the gas flow direction divided by the septum They are the adsorption and the catalyst object for emission gas purification with which it comes to support the catalyst bed which has the adsorption layer, the 3 yuan engine performance, or the oxidation engine performance of having hydrocarbon adsorption capacity. The adsorption and catalyst object ** for emission gas purification characterized by for an adsorption layer and a catalyst bed dissociating and supporting them with a certain cross section in said gas flow direction and direction of a

right angle are offered.

[0007] Moreover, adsorbent ** for emission gas purification characterized by forming the blow-by section to which it is the exhaust gas adsorbent with which it comes to support the adsorption layer which has hydrocarbon adsorption capacity, and exhaust gas blows these some honeycomb structure objects on the honeycomb structure object which has the through tube of parallel a large number divided by the septum according to this invention is offered.

[0008] Furthermore, according to this invention, the at least one above adsorption and catalyst object for emission gas purification are installed in an exhaust pipe, and the exhaust gas flow direction downstream of this adsorption and catalyst object is further provided with emission-gas-purification system ** characterized by coming to install the catalyst object with which it comes to support a catalyst bed on a honeycomb structure object.

[0009] Furthermore, according to this invention, at least one above adsorbent for emission gas purification is installed in an exhaust pipe, and the exhaust gas flow direction downstream of this adsorbent is further provided with emission-gas-purification system ** characterized by coming to install the catalyst object with which it comes to support a catalyst bed on a honeycomb structure object.

[0010] Furthermore, according to this invention, the above emission-gas-purification systems are used again. In the process in which the adsorption layer of adsorption and a catalyst object, and/or adsorbent is adsorbed, and the hydrocarbon in the exhaust gas which occurs at the time of an internal combustion engine's cold start etc. is desorbed from this adsorption layer in connection with the temperature rise by the exhaust gas of this adsorption layer Emission-gas-purification approach ** characterized by considering as the exhaust gas presentation of hyperoxia and making the hydrocarbon from which it was desorbed burn in the catalyst bed of adsorption and a catalyst object, and/or a catalyst object is offered by adding a oxidizing gas in a certain fixed period exhaust gas, or performing accommodation with a combustion air and fuel quantity. in addition, this invention -- setting -- a honeycomb structure object -- a septum -- the structure which has the divided through tube of parallel a large number is meant, and a tabular mold etc. is included.

[0011] Next, radical Motohara ** of this invention is explained. Usually, since adsorbent is heated by exhaust gas at the time of a cold start and a catalyst object is subsequently heated when adsorbent and a catalyst object are arranged sequentially from the upstream of an exhaust gas flow direction in piping, the adsorbent of the upstream always carries out a temperature rise previously from the catalyst object of the downstream. Therefore, when the adsorption layer of adsorbent adsorbs HC suitably and begins to be desorbed from it (about 80-100 degrees C), the catalyst object of the downstream is that (less than 100 degrees C) which has not reached ignition temperature yet, and HC from which it was desorbed as a result flows out out of a system with un-purifying. Moreover, even if the catalyst component was contained in the adsorption layer of adsorbent, the purification effectiveness of HC from which it was desorbed will be inadequate. This invention makes HC desorbed from the programming rate of the catalyst object of the downstream from adsorption and the catalyst object, or adsorbent of increase and the upstream using adsorption and a specific catalyst object, or specific adsorbent purify efficiently to the above problem.

[0012] If radical Motohara ** is explained taking the case of specific adsorption and catalyst object, there are few amounts of emission at the time of the idling of the start which HC generates most, and since exhaust gas flows into homogeneity comparatively in the inlet-port side of adsorption and a catalyst object, the part (henceforth the "adsorption section") with which the adsorption layer of adsorption and a catalyst object was supported will be adsorbed in much HC. Next, in this case, although the amount of emission increases in an acceleration phase, piping structure is devised or an emission guide etc. is preferably arranged just before adsorption and a catalyst object or to immediately after so that much exhaust gas may flow into the part (henceforth the "catalyst section") with which the catalyst bed of adsorption and a catalyst object was supported.

[0013] As technique different from this, the technique of making die length to some [at least] gas flow directions of the catalyst section shorter than the die length to the gas flow direction of the adsorption

section can also be taken. Moreover, the technique of making some [at least] numerical apertures of the catalyst section larger than the numerical aperture of the adsorption section is also used. Here, a numerical aperture means total of the cross section of the through tube to the cross section of a honeycomb structure object divided by the septum, i.e., the rate of gas passage area. Furthermore, the technique of making the heat capacity of the adsorption section larger than the heat capacity of the catalyst section using various approaches is also used in order to stop the programming rate of an adsorption layer (the desorption initiation stage of HC is delayed). By such technique, also in an acceleration phase, since the adsorption section of adsorption and a catalyst object will have the structure which cannot receive heating by exhaust gas easily, or cannot carry out a temperature up easily in itself, it continues adsorbing a certain fixed period HC succeeding, and results to the desorption of HC.

[0014] On the other hand, the catalyst section of adsorption and a catalyst object is steeply heated by the above-mentioned technique etc., lights at an early stage, induces big heat of reaction, and makes the catalyst object which this arranged in the downstream by convective heat transfer result in ignition certainly. That is, HC desorbed from the adsorption section as a result is purified by the catalyst object which has been arranged to the downstream at least and which is already in an ignition condition by suppressing the temperature up of the adsorption section of adsorption and a catalyst object as much as possible, and speeding up the temperature up of the catalyst object of the catalyst section and the downstream as much as possible.

[0015] When HC begins to be desorbed from the adsorption section, specifically, it is desirable to make it 150 degrees C or more of catalyst objects of the downstream have reached the temperature of 250 degrees C or more preferably. Moreover, the oxidizer which run short in order to purify HC from which it was desorbed is supplied by installation of the secondary air, or accommodation of a combustion air and fuel quantity. In addition, as an ingredient of a honeycomb structure object, when the cordierite of a ceramic, especially porosity is used, although the thing of the quality of metal may be used, since heat cannot rise in the adsorption section from the catalyst section, and the temperature of the adsorption section does not rise easily to propagation for a pile reason but the desorption stage of HC can be delayed more, it is desirable [heat conduction is bad, and].

[0016] Moreover, only an adsorption layer is supported, in the system which allots the adsorbent of the structure which a part of exhaust gas blows, a part of heat of exhaust gas can pass through adsorbent, the catalyst object of the downstream of direct adsorbent can be heated, and a catalyst object can be lit at an early stage. In this invention, the following adsorption and catalyst objects, adsorbent, and systems are used suitably.

[0017] In a honeycomb structure object with adsorption and a [catalyst object] circular cross section, what had a certain radius, supported the catalyst bed to the part which extended in the shape of a cylinder in the exhaust gas flow direction, and supported the adsorption layer in the periphery section is more desirable than a cross-section core. Moreover, the cross section of the catalyst section is desirable to especially the preignition of a catalyst in it being 5 - 80% of the cross section of a honeycomb structure object. Even when neither the cross-section configuration of a honeycomb structure object nor the cross-section configuration of the catalyst section is circular, as for the area ratio to the honeycomb structure object of the catalyst section, it is desirable to consider as 5 - 80% of range. At less than 5%, if the heat of reaction according [the area ratio to the honeycomb structure object of the catalyst section] to the preignition of the catalyst section is small, becomes what has the inadequate temperature up of the catalyst object of the downstream and exceeds 80%, the adsorption capacity of the adsorption section will fall.

[0018] Furthermore, in order to enlarge the temperature gradient of the adsorption section and the catalyst section, it is desirable to make the heat capacity of the adsorption section larger than the heat capacity of the catalyst section by increasing the amount of support of an adsorption layer which makes small the porosity of the honeycomb structure object ingredient in the adsorption section which makes high the cel consistency which enlarges rib thickness of the adsorption section and which makes the quality of the material of the adsorption section the quality of the material with big heat capacities, such

as a metal honeycomb, etc. In addition, it can say that it is reverse about the catalyst section, and the various technique of making the heat capacity of the catalyst section smaller than that of the adsorption section is used. Since technique, such as reducing the amount of support of a catalyst bed which makes rib thickness of the catalyst section small and which makes a cell consistency low especially, increases the numerical aperture of the catalyst section, consequently contributes also to the formation of low-temperature capacity of the catalyst section, and low voltage disadvantage-ization, it is desirable.

[0019] Moreover, it is desirable to make the length to some [at least] exhaust gas flow directions of the catalyst section shorter than the die length to the exhaust gas flow direction of the adsorption section, thereby, since a pressure loss becomes small while the heat capacity of the catalyst section becomes small, much exhaust gas flows at the time of engine acceleration, and the catalyst section lights at an early stage. Thus, although supporting a catalyst bed to a part of exhaust gas flow direction of a honeycomb structure object is also acquired, as shown in the perspective view (a) and sectional view (b) of drawing 3, the condition of having shortened the catalyst section is hollowing some honeycomb structure objects 15 and emasculated in a part of exhaust gas flow direction of the catalyst section 16, and it is desirable [the condition] especially to make the length to the exhaust gas flow direction of the catalyst section 16 shorter than that of the adsorption section 17.

[0020] Moreover, the catalyst section or the adsorption section may not be in the condition that either encloses another side, and the catalyst section or the adsorption section may be further divided into two or more places, respectively. Moreover, the front end section of adsorption and a catalyst object, the back end section, a part of [at least] whole cross section of the die-length direction, or a part may be the adsorption section or the catalyst section, and the adsorption section or the catalyst section does not need to be following an exhaust gas flow direction.

[0021] The adsorption layer is supported with the honeycomb structure object in which the blow-by section which [adsorbent] exhaust gas blows was formed by parts other than the blow-by section, and the blow-by section has that desirable from which the part serves as a cavity, although some of no honeycomb structure objects are supported by an exhaust gas flow direction and parallel from the exhaust gas inlet port to the outlet. Two or more places are sufficient as the cavernous section or the non-supporting section. As for the cross section of the cavernous section or the non-supporting section, it is desirable that it is less than 50% of the honeycomb structure object cross section. Moreover, the blow-by section may be formed in the through tube of a honeycomb structure object, and parallel, and predetermined makes it incline the degree of angle to a through tube, it forms, and a part of exhaust gas is good also as structure where pass the blow-by section, a part of exhaust gas flows into the adsorption layer support section, and adsorption and desorption of HC are performed.

[0022] The catalyst object for purifying HC desorbed from the adsorption section is prepared in the downstream of [system] adsorption and a catalyst object. Furthermore, it is desirable to prepare the catalyst object for preignitions in the upstream of adsorption and a catalyst object, and it is desirable to design so that the heat of reaction of an upstream catalyst object may be especially transmitted to the catalyst section of adsorption and a catalyst object quickly. As for these catalyst objects, a catalyst bed is supported on a honeycomb structure object. Moreover, it becomes [HC desorption control of the adsorption section of adsorption and a catalyst object, the preignition of the catalyst section, and/or the preignition of a catalyst object] possible by the thing of the catalyst object installed between the catalyst objects installed in adsorption and a catalyst object, its upstream, and/or the downstream, and/or in the upstream of adsorption and a catalyst object for which the heater of an electric energization heating type or EHC is further prepared in the upstream and is desirable. Moreover, the design the configuration and structure of an exhaust pipe are devised, or the preignition of a sink and the catalyst section is carried out [design] for a lot of exhaust gas than the adsorption section to the catalyst section of adsorption and a catalyst object by carrying out channeling of the exhaust gas by installation of a jammer plate, an exhaust-stream guide, etc. at the time of engine acceleration is sufficient.

[0023] Moreover, it is also a desirable system to design so that adsorbent, and adsorption and a catalyst object may be combined, it may install succeeding the inside of emission and these may demonstrate the function of adsorption and a catalyst object as a whole. In this case, although these adsorbent, and

adsorption and a catalyst object were combined, the catalyst object for purifying HC desorbed from adsorbent is required for the downstream, and it is desirable that a catalyst object is further prepared also in these upstream. On the other hand, the system which incorporated adsorbent instead of adsorption and a catalyst object is also fundamentally [as the system incorporating adsorption and a catalyst object] the same, and the catalyst object for purifying HC desorbed from adsorbent in the downstream of adsorbent is established. Furthermore, like the system incorporating the adsorption and the catalyst object mentioned above, an electric energization heating type heater can be formed, or the system considered as a configuration in which channeling of the exhaust gas is carried out, and a part of emission passes the blow-by section of adsorbent can also be used suitably. Adsorption and a catalyst object, and two or more adsorbent may be prepared, respectively.

[0024] Furthermore, in order to also raise the purification property of the whole FTP trial, it is desirable to install the catalyst object which had a certain amount of capacity in the downstream of the system which used these adsorption and a catalyst object, and/or adsorbent to the engine displacement. As an installation location of the system containing adsorption and a catalyst object, and/or adsorbent, installing near the engine is desirable because of the preignition of a catalyst bed. Moreover, since spacing of adsorption and a catalyst object and/or adsorbent, and the catalyst object installed in its upstream and lower stream of a river tells the heat of reaction generated in the catalyst bed of the upstream quickly to the catalyst bed of the downstream and promotes ignition of the catalyst bed of the downstream, it is desirable that it is close.

[0025] In order to reduce suitably HC generated at the time of a cold start, it is important that a catalyst object or the catalyst section carries out a preignition at least. usually, in the fuel rich field which may happen at the time of a cold start The combustion reaction by the catalyst object or the catalyst section cannot occur easily, and since the heating facilitatory effect by heat of reaction is not expectable in addition, either [whether the oxidizing gas installation device (for example, secondary air installation device) for introducing the gas (for example, secondary air) of an oxidizing quality from the upstream of the catalyst object nearest to an engine, or the adsorption and a catalyst object is installed, and] It is necessary to install the air-conditioning device for fuel-combustion for performing accommodation with fuel quantity and the amount of a combustion air (A/F regulatory mechanism), and to adjust an exhaust gas presentation to hyperoxia at the time of a cold start.

[0026] In addition, the exhaust gas presentation of hyperoxia here means taking the presentation by the side of hyperoxia to the exhaust gas presentation at the time of the cold start of the internal combustion engine which does not have the usual exceptional control means. If a gasoline-powered vehicle is taken for an example, it will be made to specifically shift to the Lean side of 14.6-19.0 (from an equivalent point to an oxidation side) preferably more than 14.0 (weak reduction side) with an air-fuel ratio. Thus, by making it shift to the Lean side, the oxidation activity of a catalyst object (or catalyst section) improves by leaps and bounds. In addition, since the theoretical air fuel ratio itself changes in using reformed gasoline, a methanol, etc. as a fuel, in such a case, the above-mentioned air-fuel ratio is converted by equivalent ratio λ , and it is made to shift to the Lean side preferably so that it may become the same value.

[0027] Moreover, since an exhaust gas presentation is shifted to a reduction side, even if the catalyst section or the catalyst object of the downstream has reached ignition temperature at this time, the combustion reaction of HC from which it was desorbed may be temporarily inadequate, when HC by which the adsorption section or adsorbent was adsorbed begins to be desorbed from the adsorption section or adsorbent. For this reason, it is required to consider as the exhaust gas presentation of the hyperoxia which at least one oxidizing gas installation device and/or the air-conditioning device for fuel-combustion are installed [hyperoxia] ahead of adsorption and a catalyst object, or the catalyst object (upstream) of the downstream, and may burn efficiently HC from which it was desorbed with the catalyst section or a catalyst object. That is, in order to carry out the preignition of the catalyst section or the catalyst object, a oxidizing gas installation device and/or the air-conditioning device for fuel-combustion are needed for the two purpose for the catalyst section or the catalyst object of the downstream to remove suitably HC desorbed from the adsorption section or adsorbent.

[0028] In addition, it is desirable to install at least the detection means which can detect that HC by which the adsorption section or adsorbent was adsorbed began to be desorbed from the adsorption section or adsorbent, for example, O₂ sensor, and HC sensor between adsorption and a catalyst object, or adsorbent and the catalyst object of the downstream, to detect the desorption of HC with this detection means, and to operate a oxidizing gas installation device or the air-conditioning device for fuel-combustion according to that signal. In order to carry out the preignition of the catalyst section or the catalyst object, according to the external program for avoiding the rich field which may happen beforehand according to the signal of O₂ sensor for A/F accommodation generally carried in the method of the forefront of adsorption and a catalyst object, or a catalyst object at the time of a cold start, a oxidizing gas installation device or the air-conditioning device for fuel-combustion is operated. Both a oxidizing gas installation device and the air-conditioning device for fuel-combustion may be put side by side.

[0029] Moreover, although one oxidizing gas installation device is prepared in the location of the arbitration ahead of the catalyst object (upstream) of the downstream at least in order to burn suitably HC desorbed from the adsorption section or adsorbent with the catalyst object of the downstream For the preignition of the catalyst section of the above-mentioned catalyst object nearest to an engine, or the adsorption and a catalyst object, it can use also [device / which is prepared in the upstream / oxidizing gas installation], and you may arrange separately. Furthermore, when establishing two or more oxidizing gas installation devices, you may control according to an individual and may make it interlock.

[0030] In order to make injurious ingredients, such as HC, CO, NO_x, etc. which are discharged by the internal combustion engine, remove suitably, as for the catalyst section of adsorption and a catalyst object, and a catalyst object, it is desirable that it is the thing which it comes to cover on the honeycomb structure object with which the heat-resistant oxide which contains a kind of noble metals of Pt, Pd, and the Rh(s) at least consists of heat-resistant minerals as a catalyst bed. As the quality of the material of a honeycomb structure object, it is desirable that they are the cordierite from the point of thermal resistance and thermal shock resistance and ferrite system stainless steel.

[0031] In addition, these noble metals are supported and used for the heat-resistant oxides and these multiple oxides of aluminum 2O₃, SiO₂ and TiO₂, and ZrO₂ grade. When aluminum 2O₃ which consists of specific surface area more than 100m²/g especially is used, noble metals are supported by high distribution, and a low-temperature ignition property and thermal resistance improve and are desirable. furthermore, the oxide with which oxygen storage ability of CeO₂, La 2O₃, and CeO₂-ZrO₂ grade is in a heat-resistant oxide -- 5 - 30wt% -- when it adds, stationary activity especially improves and it is desirable. the catalyst section or a catalyst -- the total amount of support of noble metals in the living body has desirable 20 - 130 g/ft³, and the amount of Rh support has the desirable range of 2 - 30 g/ft³. Moreover, it attains [low-temperature ignition] by making only Pd support three times 40 to 200 g/ft and is desirable.

[0032] As for the adsorption section or adsorbent, it is desirable that the adsorption layer which uses a zeolite as a principal component on the honeycomb structure object which consists of the above-mentioned heat-resistant minerals is covered. Although there are a zeolite, activated carbon, etc., in order to arrange adsorbent in an exhaust air system as adsorption material which can adsorb injurious ingredients, such as HC, without using a bypass method, the thermal resistance of at least 500 degrees C or more is required, and it is desirable to use a zeolite. Although any of a natural article and synthetic compounds are sufficient as a zeolite and especially a class is not limited, 40 or more things are suitably used for a Si/aluminum mole ratio thermal resistance, endurance, and in respect of hydrophobicity. Specifically, ZSM-5, USY, beta-zeolite, Silicalite, metallosilicate, etc. can use it suitably.

[0033] Moreover, a zeolite can also be used not only combining a kind but combining two or more sorts. For example, ZSM-5 in which the magnitude of the micropore of a zeolite has about 0.55nm and comparatively small pore are advantageous to adsorption of small molecules, such as a propene, and they very unsuitable for adsorption of a child like toluene or a xylene conversely. On the other hand, adsorption of small molecules, such as a propene, is disadvantageous and that of USY in which the

magnitude of micropore has the comparatively big pore which is about 0.74mm is advantageous to adsorption of the Oita children, such as toluene and a xylene. Therefore, it is also one of the suitable technique to make ZSM-5 and USY intermingled and to cover on a honeycomb structure object. Furthermore, since ZSM-5 can carry out adsorption maintenance to the comparatively high temperature of 150 degrees C in this case by classifying ZSM-5 and USY to a gas flow direction, and making it support, supporting to the upstream is desirable.

[0034] In addition, although it can be used as adsorption material even if a zeolite is independent, in order to control caulking [which carries out the from average at the time of adsorption of HC etc.], it is desirable to support the noble metals more than a kind at least of Pt, Pd, and the Rh(s), and it can reproduce, without the adsorption capacity of a zeolite falling by this. As noble metals supported by the zeolite, Pd is the cheapest and regenerative capacity's is highly desirable. Moreover, as for the support approach of noble metals, it is desirable to be based on an ion-exchange method in respect of thermal stability. Furthermore, the amount of support of noble metals has 40g [5-]/desirable ft³ (honeycomb volume) in respect of cost and regenerative capacity. When supporting a zeolite on a honeycomb structure object, 5 - 20wt% aluminum 2O₃ and the inorganic binder of SiO₂ may be included if needed, and it is supported firmly, without this spoiling adsorption capacity, such as HC.

[0035] As mentioned above, although noble metals have not only the regenerative capacity of a zeolite but a catalysis as a result when a zeolite is made to support noble metals, it can be easy to condense the noble metals in a zeolite, and the catalyst bed which is made to contain a catalyst component equivalent to the catalyst bed used for the adsorption layer which consists of a zeolite with a catalyst object since endurance is inadequate as a catalyst, or contains a catalyst component on the surface of an adsorption layer can be covered, and it can use. In this case, since the adsorption section or adsorbent will contain a durable catalyst component, it shows [decontamination capacity] suitably also at the time of the stationary transit after a cold start and is desirable. Moreover, since adding a catalyst component has the effectiveness which controls caulking [of a zeolite], there is not necessarily no need of adding noble metals in a zeolite.

[0036] Moreover, since including at least one sort of ion of IB group element (Cu, Ag, Au) of a periodic table in a zeolite also raises HC adsorption capacity of a zeolite, it is desirable. In this case, since effectiveness is thin to the improvement in HC adsorption capacity when the content of the above-mentioned ion is small, as for the content of the above-mentioned ion of a zeolite, it is desirable that it is 20% or more to aluminum atom in a zeolite, and it is more desirable in it being 40% or more. These ion may be combined with the noble metals and arbitration which carried out point **, and may be included in a zeolite. furthermore, the ion of the above-mentioned IB group element -- in addition, at least a kind of ion chosen from the various ion of Mg, calcium, Sr, Ba, Y, La, Ti, Ce, Mn, Fe, Cr, nickel, and Zn -- thermal resistance improves and is desirable when a kind of ion of the ion of Mg, calcium, Fe, and Cr is made to contain in a zeolite at least preferably.

[0037] In the adsorption section or adsorbent, as one of the desirable examples which cover a catalyst bed on the surface of an adsorption layer High silica content zeolites, such as ZSM-5, USY, beta-zeolite, etc. with which noble metals were supported by the surface of a honeycomb structure object, are covered as the 1st layer. Furthermore, layer type the adsorption and the catalyst object, or adsorbent which covered aluminum₂O₃-CeO₂ multiple oxide with which noble metals were supported as the 2nd layer is mentioned to the front face. Such layer type adsorption and a catalyst object, or adsorbent has the effectiveness of the pre dryer which adsorbs alternatively H₂O by which aluminum 2O₃ which is the principal component of the 2nd layer is contained in the exhaust gas at the time of a cold start, and raises adsorption of HC which the 1st layer takes charge of. In addition, it is heated from the 2nd layer which contains the catalyst component by the side of a surface with the rise of an exhaust gas temperature, and when desorbed from HC to which the zeolite component of the 1st layer stuck, the catalyst of the 2nd layer acts suitably. When this HC etc. ****s, it is indispensable to have considered as the exhaust gas presentation of hyperoxia by addition of a oxidizing gas or accommodation of the amount and fuel quantity of a combustion air, and, thereby, the 2nd-layer catalysis improves by leaps and bounds.

[0038] In addition, even if the catalyst component with which noble metals were supported, and the

zeolite component are supported with the condition of having been intermingled instead of a layer type by the honeycomb structure object, it acts on it comparatively good. The weight ratio of a zeolite component and a catalyst component is 50-85:15-50, and it is desirable that many zeolite components are included. As for the amount of support to a honeycomb structure object, it is desirable that a zeolite component considers as the range 0.05-0.40g [cc] /and whose catalyst component are 0.02-0.20g/cc. [0039] It is also desirable to arrange at least one electric energization heating type heater (for it to be called "EH" below Electrical Heater;) in order to attain the preignition of the catalyst section or a catalyst object in an exhaust air system in this invention. It is desirable to prepare and constitute the electrode for energization on the honeycomb structure object which consists of quality of a heat-resistant metal, such as a ferrite, a pressure loss and in respect of thermal resistance, and when it covers the catalyst bed which consists of a heat-resistant inorganic oxide which contains noble metals at least and it is further use for it as EHC (namely, catalyst object of an electric energization heating method) on this EH, since EH can reduce the power which borrows the assistance of the heat of reaction of a catalyst and heating of a heater takes, it is desirable.

[0040] In the emission-gas-purification approach of this invention, although ozone, O₂-, the secondary air, etc. can be used as gas of an oxidizing quality that what is necessary is just to introduce the gas of an oxidizing quality in order to activate the catalyst section or the catalyst object in a purification system, the secondary air which can be introduced with simple equipments, such as an air pump, among these is the most desirable. Since heating by the exhaust air heat of exhaust gas is quick when adsorption and the catalyst object, or the catalyst object is arranged near the engine, the stage to introduce oxidizing quality gas may start installation to coincidence substantially with the time of engine starting. Moreover, as for an introductory halt stage, the time of O₂ sensor for A/F accommodation operating and being operated by equivalent ratio with engine warming up, serves as a standard, and, in the case of O₂ with a heater sensor, it is a time of having passed about 40 to 140 seconds after an engine crank for 20 to 50 seconds after an engine crank in the case of heater nothing O₂ sensor.

[0041] As for the introductory stage of the oxidizing gas introduced on the other hand in order to make HC desorbed from the adsorption section or adsorbent burn efficiently with the catalyst section or the catalyst object of the downstream, it is desirable to detect with the detection means (O₂ sensor, HC sensor, etc.) of adsorption and a catalyst object, or the adsorbent downstream. The approach of feeding back and controlling the output from a detection means can also be used for the amount of installation to adsorption and a catalyst object, or the catalyst object of the downstream that an exhaust gas presentation should just become hyperoxia. Although it depends for an introductory initiation stage also on the location of adsorbent since it begins to be desorbed from HC when the temperature of the adsorption section or adsorbent generally exceeds 80-100 degrees C, installation is started in 50 seconds after after an engine crank, and a halt of installation is a time of about 40 to 140 seconds passing after an engine crank.

[0042] When using EH and EHC together and an electrical potential difference is impressed to installation and coincidence of a oxidizing gas, HC from which it was desorbed from the adsorption section is efficiently purified by the catalyst section, the catalyst object of the lower stream of a river, etc., and is desirable. Although the amount of installation of oxidizing quality gas changes also with engine displacements, let it be 50 - 300 l/min extent. Since the catalyst section or a down-stream catalyst object will be cooled when it introduces beyond the need, it is most desirable to introduce so that an air-fuel ratio may become near the equivalent point. Also as fixed, it may carry out adjustable [of the amount of oxidizing gas installation] suitably.

[0043] The same effectiveness is acquired also by the approach of adjusting the engine operating method other than the approach of introducing oxidizing quality gas, i.e., the amount and fuel quantity of a combustion air, and acquiring the exhaust gas presentation of hyperoxia. After engine ignition in for example, open loop control (O₂ sensor use is not carried out) To the air content detected with the intake air flow sensor etc. [whether fuels fewer than a theoretical fuel are introduced and] Or using O₂ sensor, beforehand, there is a certain fixed period, for example, the approach of controlling to the Lean side etc., using the PEGO sensor from which a computer adjusts or a sensor output changes with air-fuel ratios

linearly further so that it may control to a certain fixed period, for example, Lean, side.

[0044] the time of ignition in an engine -- the fuel from the point of operability -- since a rich condition can be taken, in addition to the usual system, the equipment which can control an exhaust gas presentation using these approaches is needed. Although the approach of controlling an exhaust gas presentation using a sensor is excellent in respect of precision, it takes time amount to carry out the sensor [itself] warming up. this uses a sensor with a heater etc. -- more -- or -- becoming -- although improved, in order to acquire the exhaust gas presentation of hyperoxia early comparatively after an engine crank, it is desirable to introduce a oxidizing gas or to use control units other than a sensor. Moreover, it is also one of the suitable technique to use together the approach of both oxidizing gas installation and accommodation of the air content for combustion and fuel quantity, and to acquire the exhaust gas presentation of hyperoxia.

[0045]

[Example] Hereafter, although this invention is further explained to a detail based on an example, this invention is not limited to these examples.

[0046] [Production of adsorption and catalyst object]:adsorption, and the catalyst object I; diameter 144mmphi, the nature honeycomb structure object of the cordierite by NGK Insulators, Ltd. with a die length of 100mm (150 micrometers of rib thickness) Gamma-aluminum 2O3 and 0.23g /of CeO(s)2 (weight ratio 70:30) are supported cc in the cylinder section with a radius [of 44mm], and a shaft-orientations die length [of a through tube] of 100mm from the central point of the cross section of cel consistency 400 cel / square inch. Subsequently Rh was supported 80g / ft3 so that it might become the ratio of Pd, Pt, and6:5:1, and it calcinated at 550 degrees C, and considered as the catalyst bed. Next, ZSM-5 [0.15g / /] made from The PQ Corporation (Si/aluminum mole ratio = 280) was supported cc in the periphery section, and it calcinated at 550 degrees C, and considered as the adsorption layer. As shown in drawing 1 as mentioned above, the adsorption and the catalyst object I with which the catalyst section 16 with which the catalyst bed was supported was formed in the cross-section center section of the honeycomb structure object 15, and the adsorption section 17 with which the adsorption layer was supported by the periphery section was formed were acquired.

[0047] Adsorption and the catalyst object II; the same honeycomb structure object as above-mentioned adsorption and catalyst object I was used, ZSM-5 were supported and calcinated like adsorption and the catalyst object I from the core of the cross section in the cylinder section with a radius [of 52mm], and a shaft-orientations die length [of a through tube] of 100mm, and the catalyst bed was supported and calcinated like adsorption and the catalyst object I in the periphery section. As shown in drawing 2 as mentioned above, the adsorption and the catalyst object II with which the adsorption section 17 with which the adsorption layer was supported was formed in the cross-section center section of the honeycomb structure object 15, and the catalyst section 16 with which the catalyst bed was supported by the periphery section was formed were acquired.

[0048] a part with a radius [from the core of the cross section of the same honeycomb structure object as adsorption, the catalyst object III; above-mentioned adsorption, and the catalyst object I / of 44mm], and a shaft-orientations die length [of a through tube] of 50mm -- hollowing -- adsorption and a catalyst -- the body and its function -- it considered as support. Next, Pd(NO3) 3 water solution was used for gamma-aluminum 2O3 and CeO2 (weight ratio 70:30), it sank in, Pd was calcinated at 550 degrees C after desiccation, and Pd support gamma-aluminum 2O3 and CeO2 multiple oxide was obtained. 0.1g /of this multiple oxide was supported cc into the part (part extended from the hollowed part to through tube shaft orientations) with a radius [of 44mm], and a shaft-orientations die length [of a through tube] of 50mm from the core of the cross section of the above-mentioned adsorption and support for catalysts, and it calcinated at 550 degrees C, and considered as the catalyst bed. The amount of Pd support of a catalyst bed became 150 g/ft3. Next, 2(NH3) Pt (NO2)2 was used for ZSM-5, it processed at 90 degrees C for 4 hours, the ion exchange of the Pt was carried out, it calcinated at 550 degrees C after desiccation, and Pt-ion-exchange zeolite powder was obtained. This powder was supported in the periphery section of the part which supported the above-mentioned catalyst bed, and it calcinated at 550 degrees C, and could be the 1st layer. In the amount of support of the 1st layer, 0.15g

[cc] /and the amount of Pt(s) became 33.3 g/ft³. Next, the powder which pre doped Rh was similarly supported and calcinated on the 1st layer to gamma-aluminum 2O₃, and it could be the 2nd layer. The amount of support of the 2nd layer is 0.05g/cc. The amount of Rh(s) became 6.7 g/ft³. Furthermore, the powder which pre doped Pd was supported and calcinated on the 2nd layer to gamma-aluminum 2O₃, and it could be the 3rd layer. In the amount of support of the 3rd layer, 0.03g [cc] /and the amount of Pd became 40 g/ft³. As shown in the perspective view of drawing 3 (a), and the sectional view of (b) as mentioned above The catalyst section 16 with which the catalyst bed was supported is formed in the cross-section center section of the honeycomb structure object 15 with which it was hollowed and the die length (exhaust gas flow lay length) of the shaft orientations of a through tube became short as compared with the periphery section. The adsorption and the catalyst object III with which the adsorption section 17 with which the adsorption layer of the double layer structure which also contained the catalyst component in the periphery section was supported was formed were acquired.

[0049] Adsorption and the catalyst object IV; respectively the catalyst bed was supported, four points of dividing a with a radius of 40mm periphery top into four equally were calcinated like adsorption and the catalyst object I, in the four cylinder sections with a central radius [of 25mm], and a shaft-orientations die length [of a through tube] of 100mm, from the core of the cross section of the same honeycomb structure object as above-mentioned adsorption and catalyst object I, and ZSM-5 were supported and calcinated into the remaining part. As shown in drawing 4 as mentioned above, two or more formation of the catalyst section 16 with which the catalyst bed was supported by the honeycomb structure object 15 was carried out, and the adsorption and the catalyst object IV with which the adsorption section 17 with which the adsorption layer was supported by other parts was formed were acquired.

[0050] Adsorption and the catalyst object V; It borders on the orthotomic which classifies into 64mm and 80mm the straight line prolonged in the diameter direction of the cross section using the same honeycomb structure object as above-mentioned adsorption and catalyst object I. In the small cross-section section of the inside made into the small cross-section section and the large cross-section section for 2 minutes, the catalyst bed was supported and calcinated like adsorption and the catalyst object I, in the large cross-section section, like adsorption and the catalyst object I, ZSM-5 were supported and the honeycomb structure object was calcinated. As shown in drawing 5 as mentioned above, the adsorption and the catalyst object V with which the catalyst section 16 with which the catalyst bed was supported was formed in one boundary side which carries out the cross section of the honeycomb structure object 15 for 2 minutes, and the adsorption section 17 with which the adsorption layer was supported at another side was formed were acquired.

[0051] Adsorption and the catalyst object VI; The same honeycomb structure object as above-mentioned adsorption and catalyst object I is used. Into two parts which contact and counter in the straight line passing through the core of the cross section in the central point of the four parts carried out 4 ****s, the catalyst bed was supported and calcinated like adsorption and the catalyst object I, and ZSM-5 were supported and calcinated like adsorption and the catalyst object I into the two remaining parts. The adsorption and the catalyst object VI with which the catalyst section 16 from which the catalyst bed was supported with the straight line passing through the core of the cross section of the honeycomb structure object 15 by two parts which contact and counter in the central point of the four parts carried out 4 ****s as shown in drawing 6 as mentioned above was formed, and the adsorption section 17 with which the adsorption layer was supported by the two remaining parts was formed were acquired.

[0052] the nature honeycomb structure object of cordierite (100 micrometers of rib thickness, cel consistency 400 cel / square inch) of adsorption and the catalyst object VII; outer diameter phi of 144mm, bore 45mmphi, the bell shape nature honeycomb structure object of cordierite with a die length of 100mm (300 micrometers of rib thickness, cel consistency 300 cel / square inch) and outer-diameter 44mmphi, and the shape of a cylinder with a die length of 100mm -- a low expansion ceramic jointing material for corrugated fibreboard -- joining -- adsorption and a catalyst -- the body and its function -- it considered as support. On the honeycomb structure object of the 300 cels / square inch which constitutes the periphery section of this support, the catalyst bed was supported and calcinated like adsorption and the catalyst object I, and ZSM-5 were supported and calcinated like adsorption and the catalyst object I

on the honeycomb structure object of the 400 cels / square inch which constitutes a center section. As shown in drawing 7 as mentioned above, the adsorption section 17 with which the adsorption layer was supported by the part with the high cel consistency of the cross-section center section of the honeycomb structure object 15 was formed, and the adsorption and the catalyst object VII with which the catalyst section 16 with which the catalyst bed was supported at the part with the low cel consistency of the periphery section was formed were acquired.

[0053] a part with the [production of adsorbent]:adsorbent I; diameter phi of 144mm, a radius [from the central point of the cross section of the nature honeycomb structure object of the cordierite by NGK Insulators, Ltd. with a die length of 100mm (150 micrometers of rib thickness, cel consistency 400 cel / square inch) / of 44mm], and a shaft-orientations die length [of a through tube] of 100mm -- hollowing -- the support for adsorbent -- carrying out -- adsorption and the catalyst object I -- the same -- carrying out -- ZSM-5 -- it supported and calcinated. As shown in drawing 8 as mentioned above, the adsorbent I in which the cross-section center section of the honeycomb structure object 15 was blown, and the section 18 was formed was obtained. That is, Adsorbent I blows the catalyst section of adsorption and the catalyst object I, and is taken as the section.

[0054] Adsorbent II; four parts with a central radius [points / four / of dividing a with a radius of 40mm periphery top into four equally from the core of the cross section of the same honeycomb structure object as above-mentioned adsorption and catalyst object I / of 25mm], and a shaft-orientations die length [of a through tube] of 100mm were hollowed, respectively, it considered as the support for adsorbent, and ZSM-5 were supported and calcinated like adsorption and the catalyst object I. As shown in drawing 9 as mentioned above, the adsorbent II which blows the honeycomb structure object 15 and by which two or more formation of the section 18 was carried out was obtained. That is, Adsorbent II blows the catalyst section of adsorption and the catalyst object IV, and is taken as the section.

[0055] Adsorbent III; on the nature honeycomb structure object of cordierite of the cube configuration whose one side is 100mm, two scooping outs whose cross sections penetrated to the shaft orientations and the perpendicular direction of a through tube are 50mmx20mm were prepared at intervals of 20mm, it considered as the support for adsorbent, and SM-5 were supported and calcinated like adsorption and the catalyst object I. As shown in drawing 10 as mentioned above, the adsorbent III in which the blow-by section 18 penetrated to the shaft orientations and the perpendicular direction of a through tube to the honeycomb structure object 15 was formed was obtained.

[0056] [Production of catalyst object]:catalyst objects I, II, III, and IV; Diameter 93mmphi, Die length of 33mm (catalyst object I), diameter phi99mmphi, die length of 99mm (catalyst object II), Diameter phi144mmphi, die length of 100mm (catalyst object III), and diameter phi76mmphi, Four kinds of nature honeycomb structure objects of the cordierite by NGK Insulators, Ltd. with a die length of 88mm (catalyst object IV) (150 micrometers of rib thickness) Gamma-aluminum 2O₃ and 0.23g /of CeO(s)₂ (weight ratio 70:30) were supported cc into the through tube number 400 cel / square inch, subsequently, Rh was supported three times 80 g/ft so that it might become the ratio of Pd, Pt, and 6:5:1, and it calcinated at 550 degrees C, and the catalyst objects I, II, III, and IV were acquired.

[0057] [Preparation of an electric energization heating type heater]: It added and mixed so that it might become the presentation of Fe-18Cr-8aluminum-0.05B-0.5Y₂O₃ for Fe powder with a mean particle diameter of 44 micrometers or less, Cr-30aluminum powder (% of the weight), Fe-50aluminum powder (% of the weight), Fe-20B powder (% of the weight), and Y₂O₃ powder. 1g of oleic acid was added as an antioxidant by having used per 100g of this mixture, and methyl cellulose 4g as the organic binder, and it mixed. Thus, after preparing a plastic matter, extrusion molding of the cylindrical shape-like honeycomb Plastic solid was carried out, and the acquired honeycomb Plastic solid was dried at 90 degrees C among atmospheric air for 16 hours, and subsequently to 1325 degrees C, under the hydrogen ambient atmosphere, it held for 2 hours and sintered. Furthermore, heat treatment was performed for 30 minutes at 1150 degrees C among air, and the honeycomb structure object was acquired. The porosity of the acquired honeycomb structure object was 3%.

[0058] To the honeycomb structure object of the cel consistency 450 cel / square inch which consists of 0.1mm in 25mm in outer-diameter 93mmphi obtained by the above-mentioned approach, and thickness,

and septum thickness, and a hexagon-head cel, by the grinding process using a band saw, as shown in drawing 25, the slit 12 was formed in the direction parallel to the shaft of a through tube, as the number of cels between six places and a slit became seven pieces, and it adjusted so that resistance of a heater might be set to 50mohm. Subsequently, on the heater, the same catalyst bed as the catalyst object I was covered, and the electrode 11 was arranged at the heater, and it contained, taking this can and an insulation in the can made from SUS. The sensitive volume of a heater was 0.13l.

[0059] [Emission-gas-purification structure of a system]: The emission-gas-purification system as shown below in **** for the adsorption and the catalyst object acquired by the above, adsorbent, a catalyst object, and electric energization heating type heaters was constituted. In addition, in order to clarify distinction with the Roman numerals which show the class of adsorption and a catalyst object, adsorbent, and catalyst object, and the reference mark in drawing, in explanation of the following systems, the reference mark in drawing attached and described the parenthesis ().

[0060] System A; as shown in drawing 11, adsorption and catalyst object I (21) were installed in the upstream of the emission way from an engine (1), and the catalyst object II (42) was installed in the downstream. Moreover, between adsorption and engine (1) and catalyst object I (21), the secondary air installation hole for promotion of ignition (3) was installed in O2 sensor for A/F accommodation (2), and the downstream at the upstream. The distance to adsorption and catalyst object I (21) set spacing of 600mm, adsorption and catalyst object I (21), and the catalyst object II (42) to 30mm from the engine manifold outlet. Furthermore, the catalyst object III (not shown) was installed in the location of 1200mm from the engine manifold outlet.

[0061] As shown in drawing 12, System B; on the emission way from an engine (1) It installs from an engine (1) side in order of catalyst object I(41) adsorption and the catalyst object III (23), and the catalyst object II (42). Between engine (1) and catalyst object I (41) The secondary air installation hole for promotion of ignition (3) was installed in the upstream at O2 sensor for A/F accommodation (2), and the downstream. The distance to catalyst object I (41) set each spacing of catalyst object I(41) adsorption and [600mm and] the catalyst object III (23), and the catalyst object II (42) to 30mm from the engine manifold outlet. Furthermore, the catalyst object III (not shown) was installed in the location of 1200mm from the engine manifold outlet.

[0062] As shown in drawing 13, System C; on the emission way from an engine (1) An adsorption [from an engine (1) side], and catalyst object III(23) electrical-and-electric-equipment energization heating type heater (50), It installed in order of the catalyst object II (42), and the secondary air installation hole for promotion of ignition (3) was installed [the upstream] between an engine (1), and adsorption and a catalyst object III (23) at O2 sensor for A/F accommodation (2), and the downstream. The distance to adsorption and the catalyst object III (23) set each spacing of an adsorption and 600mm and catalyst object III(23) electrical-and-electric-equipment energization heating type heater (50) and the catalyst object II (42) to 30mm from the engine manifold outlet. Furthermore, the catalyst object III (not shown) was installed in the location of 1200mm from the engine manifold outlet.

[0063] System D; as shown in drawing 14, it considered as the same configuration as the above-mentioned system C except having installed catalyst object I (41) further between a secondary air installation hole (3), and adsorption and a catalyst object III (23). However, from the engine manifold outlet, distance to catalyst object I (41) was set to 600mm, and spacing of catalyst object I (41), and the adsorption and a catalyst object III (23) was set to 30mm.

[0064] System E; as shown in drawing 15, it considered as the same configuration as the above-mentioned system D except having arranged another electric energization heating type heater (50') further between catalyst object I (41), and adsorption and a catalyst object III (23). In addition, each spacing of a catalyst object I(41) electrical-and-electric-equipment energization heating type heater (50'), and the adsorption and a catalyst object III (23) was set to 30mm.

[0065] a system -- F --; -- drawing 16 -- being shown -- as -- an engine -- (-- one --) -- from -- emission -- a way -- the upstream -- a catalyst -- the body -- I -- (-- 41 --) -- installing -- the -- the downstream -- adsorption - a catalyst -- the body -- I -- gas -- a flow direction -- a perpendicular direction -- having halved -- adsorption - a catalyst -- the body -- I -- '(21)' -- and -- adsorption - a catalyst -- the body -- I --

" (21") -- adjoining -- having installed . Furthermore, the catalyst object II (42) was installed in the downstream. Moreover, between engine (1) and catalyst object I (41), the secondary air installation hole for promotion of ignition (3) was installed in O2 sensor for A/F accommodation (2), and the downstream at the upstream. an engine -- a manifold -- an outlet -- a catalyst -- the body -- I -- (-- 41 --) -- up to -- distance -- 600 -- mm -- a catalyst -- the body -- I -- (-- 41 --) -- adsorption - a catalyst -- the body -- I -- ' (21)' -- adsorption - a catalyst -- the body -- I -- " (21)" -- a catalyst -- the body -- II -- (-- 42 --) -- each -- spacing -- 30mm -- having carried out . Furthermore, the catalyst object III (not shown) was installed in the location of 1200mm from the engine manifold outlet.

[0066] System G; as shown in drawing 17 , it installed in the emission way from the upstream from the engine (1) in order of catalyst object I(41) adsorption and catalyst object V (25), and the catalyst object II (42). Although the exhaust pipe (4) was 50mm in bore, it was designed in each installation section of catalyst object I(41) adsorption and catalyst object V (25), and the catalyst object II (42) so that a path might be expanded caudad. Adsorption and catalyst object V (25) were installed so that the upper part might turn into the catalyst section (16) and the lower part might turn into the adsorption section (17). Moreover, between engine (1) and catalyst object I (41), the secondary air installation hole for promotion of ignition (3) was installed in O2 sensor for A/F accommodation (2), and the downstream at the upstream. The distance to catalyst object I (41) set each spacing of catalyst object I(41) adsorption and [600mm and] catalyst object V (25), and the catalyst object II (42) to 30mm from the engine manifold outlet. Furthermore, the catalyst object III (not shown) was installed in the location of 1200mm from the engine manifold outlet.

[0067] System H; as shown in drawing 18 , it installed in the emission way from the upstream from the engine (1) in order of catalyst object I(41) adsorption and the catalyst object III (23), and the catalyst object II (42). The bore of an exhaust pipe (4) is rapidly narrowed down before and behind adsorption and the catalyst object III (23), spacing of the both-ends side of the adsorption section (17) and the wall of an exhaust pipe (4) which were formed in the periphery section of adsorption and the catalyst object III (23) is 10mm, and exhaust gas has stopped being able to flow easily as compared with the catalyst section (16) formed in the center section in the adsorption section (17). Moreover, between engine (1) and catalyst object I (41), the secondary air installation hole for promotion of ignition (3) was installed in O2 sensor for A/F accommodation (2), and the downstream at the upstream. The distance to catalyst object I (41) set each spacing of catalyst object I(41) adsorption and [600mm and] the catalyst object III (23), and the catalyst object II (42) to 30mm from the engine manifold outlet. Furthermore, the catalyst object III (not shown) was installed in the location of 1200mm from the engine manifold outlet.

[0068] System I; as shown in drawing 19 , it installed in the emission way from the upstream from the engine (1) in order of adsorption and catalyst object I (21), and the catalyst object II (42). It extracted to the catalyst section (16) formed in the center section of adsorption and catalyst object I (21) in emission ahead of adsorption and catalyst object I (21) (upstream), and the exhaust-stream guide (5) for making it increase as compared with the adsorption section (17) by which the amount of emission of the catalyst section (16) was formed in the periphery section was prepared in the interior of an exhaust pipe (4). Moreover, between adsorption and engine (1) and catalyst object I (21), the secondary air installation hole for promotion of ignition (3) was installed in O2 sensor for A/F accommodation (2), and the downstream at the upstream. The distance to adsorption and catalyst object I (21) set spacing of 600mm, adsorption and catalyst object I (21), and the catalyst object II (42) to 30mm from the engine manifold outlet. Furthermore, the catalyst object III (not shown) was installed in the location of 1200mm from the engine manifold outlet.

[0069] As shown in drawing 20 , adsorption and the catalyst object II (22) are installed instead of adsorption and the catalyst object I of the above-mentioned system I. System J; inside an exhaust pipe (4) It is made easy to flow in the catalyst section (16) formed in the periphery section of adsorption and the catalyst object II (22) in emission ahead of adsorption and the catalyst object II (22) (upstream). The exhaust-stream guide (6) for making it the amount of emission of the catalyst section (16) increase as compared with the adsorption section (17) formed in the center section was prepared. Other configurations are the same as that of the above-mentioned system I.

[0070] System K; as shown in drawing 21 , it installed in the emission way from the upstream from the engine (1) in order of catalyst object I(41) adsorption and the catalyst object III (23), and the catalyst object IV (44). Adsorption and the catalyst object III (23) have been arranged so that the end face of the side which has the ***** cavernous section formed in the part extended to the exhaust gas flow direction may serve as the downstream from the catalyst section (16) of a cross-section center section, and where the catalyst object IV (44) is inserted in the cavernous section 20mm, it has been arranged. Once all HC desorbed from the adsorption section (17) of adsorption and the catalyst object III (23) flowed to hard flow, the exhaust pipe (4) was designed so that the catalyst object IV (44) might be passed. Moreover, between engine (1) and catalyst object I (41), the secondary air installation hole for promotion of ignition (3) was installed in O₂ sensor for A/F accommodation (2), and the downstream at the upstream. The distance to catalyst object I (41) set each spacing of catalyst object I(41) adsorption and [600mm and] the catalyst object III (23), and the catalyst object IV (44) to 30mm from the engine manifold outlet. Furthermore, the catalyst object III (not shown) was installed in the location of 1200mm from the engine manifold outlet.

[0071] System L; as shown in drawing 22 , it installed in the emission way from the upstream from the engine (1) in order of catalyst object I(41) adsorbent I(31) adsorption and catalyst object I (21), and the catalyst object II (42). Moreover, between engine (1) and catalyst object I (41), the secondary air installation hole for promotion of ignition (3) was installed in O₂ sensor for A/F accommodation (2), and the downstream at the upstream. The distance to catalyst object I (41) set each spacing of 600mm and catalyst object I(41) adsorbent I(31) adsorption and catalyst object I (21), and the catalyst object II (42) to 30mm from the engine manifold outlet. Furthermore, the catalyst object III (not shown) was installed in the location of 1200mm from the engine manifold outlet.

[0072] System M; as shown in drawing 23 , adsorbent I (31) in which the cross-section center section was blown and the section (18) was formed instead of adsorption and the catalyst object III of the above-mentioned system B was installed. Other configurations are the same as that of the above-mentioned system B.

[0073] System N; as shown in drawing 24 , the adsorbent III (33) in which the blow-by section penetrated to the shaft orientations and the perpendicular direction of a through tube of a honeycomb structure object was formed instead of adsorption and the catalyst object III of the above-mentioned system B was installed. In addition, Adsorbent III (33) was installed in the exhaust pipe so that it might blow with an exhaust gas flow direction and the shaft orientations of the section might become parallel, and the through tube end face opened it wide so that a part of exhaust gas might flow out of the blow-by section into a through tube. Other configurations are the same as that of the above-mentioned system B.

[0074] [Evaluation of an emission-gas-purification system]: That the emission-gas-purification engine performance of above-mentioned system A-N should be evaluated, the test car of the displacement of 2000 cc and a 4-cylinder engine loading was used, and the FTP trial (LA-4 mode) was carried out. In addition, in order to obtain the exhaust gas of hyperoxia, the secondary air was introduced by 100 l/min for 90 seconds from the engine crank from each introductory hole with the air pump in simple.

Moreover, in the case of the system which contains an electric energization heating type heater in a configuration, the injection of the power to an electric energization heating type heater was performed using 12V dc-battery, and it energized by 2kW for 30 seconds after after [of an after / an engine crank] 30 seconds. Exhaust gas was extracted by the CVS method and computed the emission value. A test result is shown in Table 1.

[0075]

[Table 1]

システム	HCエミッション	
	B a g 1 A (g)	トータル (g/mile)
A	0. 8 8	0. 0 6 4
B	0. 5 1	0. 0 4 2
C	0. 3 6	0. 0 3 3
D	0. 3 5	0. 0 3 0
E	0. 3 3	0. 0 2 8
F	0. 8 5	0. 0 5 7
G	0. 7 9	0. 0 5 3
H	0. 4 8	0. 0 4 0
I	0. 9 2	0. 0 6 6
J	0. 9 3	0. 0 7 0
K	0. 5 4	0. 0 4 5
L	0. 5 0	0. 0 4 4
M	0. 6 5	0. 0 4 8
N	0. 7 1	0. 0 5 1

[0076] At the time of the FTP trial of the above-mentioned system C, [Measurement of temperature distribution] : K thermocouple From the inlet-port end face of the catalyst section of adsorption and the catalyst object III, the location of 10mm inside (location A), From the outlet end face of the adsorption section, it set to the location (location C) of 10mm inside, respectively from the location (location B) of 10mm inside, and the inlet-port end face of the catalyst object II, and the temperature distribution at the time of a FTP start (temperature of the location B when a location A reaches 100 degrees C, 200 degrees C, and 300 degrees C, and a location C) were measured. The result is shown in Table 2. It turns out that temperature is lower than the inlet port of the catalyst object II in which the direction of the adsorption section outlet of the adsorption and the catalyst object III located ahead (upstream) from this result is located back (downstream).

[0077]

[Table 2]

位置 A	位置 B	位置 C
1 0 0 °C	5 8 °C	7 2 °C
2 0 0 °C	7 6 °C	1 2 5 °C
3 0 0 °C	9 4 °C	2 0 6 °C

[0078]

[Effect of the Invention] As explained above, according to this invention, the injurious ingredient in the exhaust gas discharged by the internal combustion engine, especially HC which carries out extensive generating at the time of a cold start can be purified efficiently.

[Translation done.]

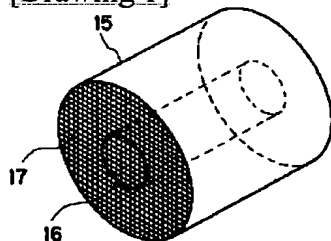
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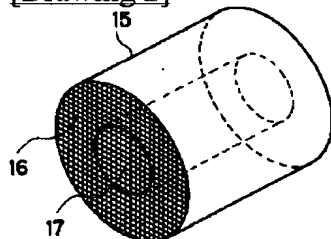
1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DRAWINGS

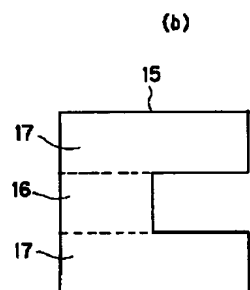
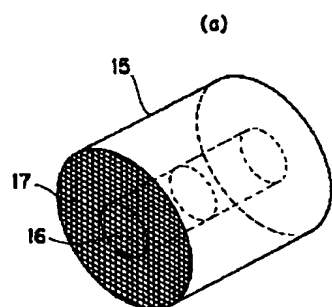
[Drawing 1]



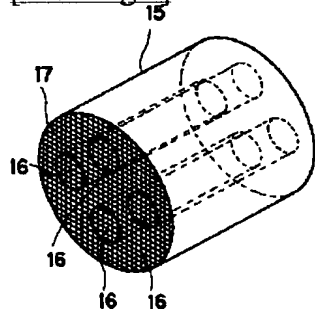
[Drawing 2]



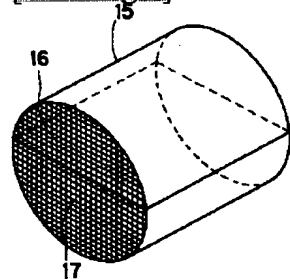
[Drawing 3]



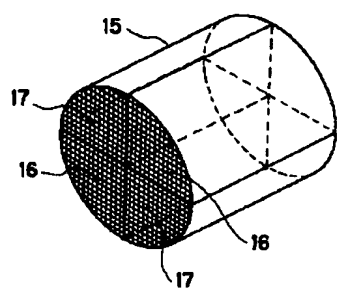
[Drawing 4]



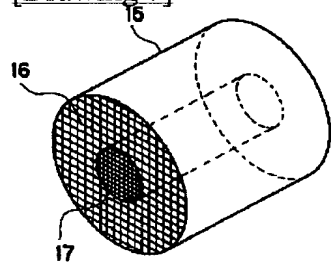
[Drawing 5]



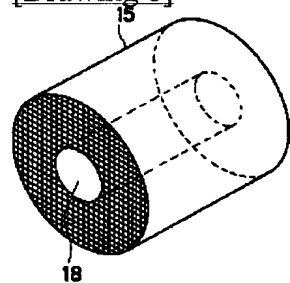
[Drawing 6]



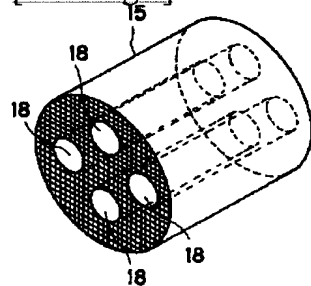
[Drawing 7]



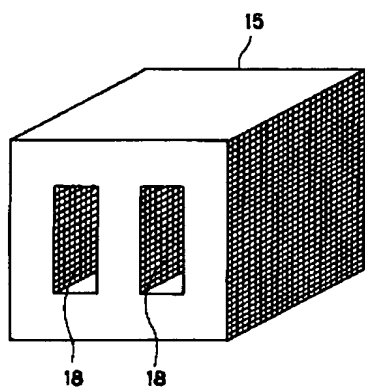
[Drawing 8]



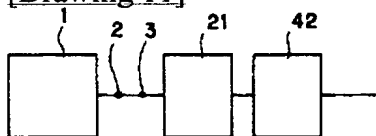
[Drawing 9]



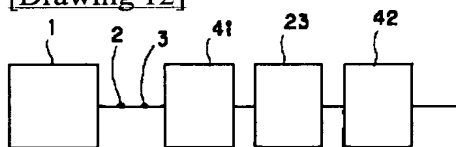
[Drawing 10]



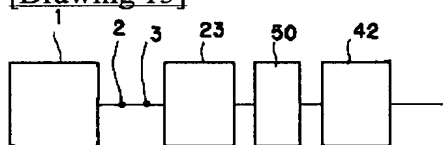
[Drawing 11]



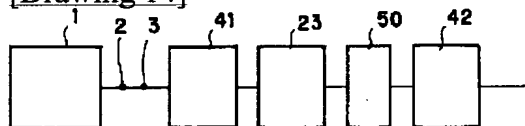
[Drawing 12]



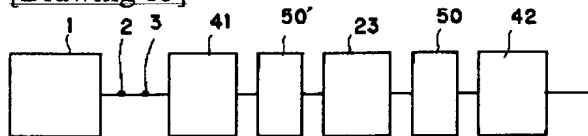
[Drawing 13]



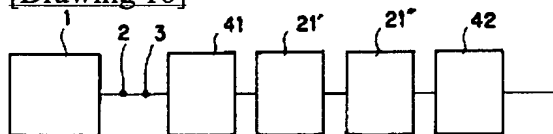
[Drawing 14]



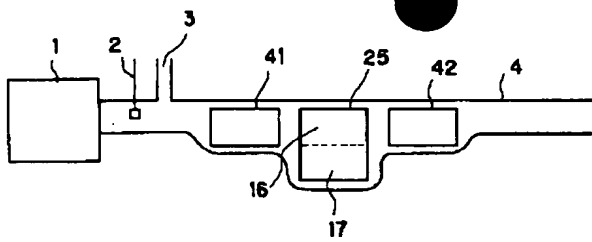
[Drawing 15]



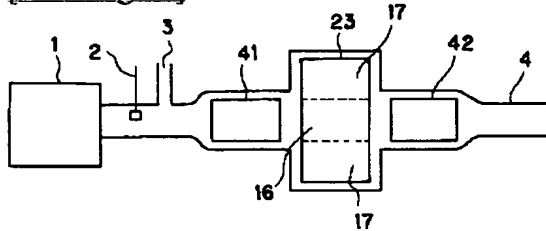
[Drawing 16]



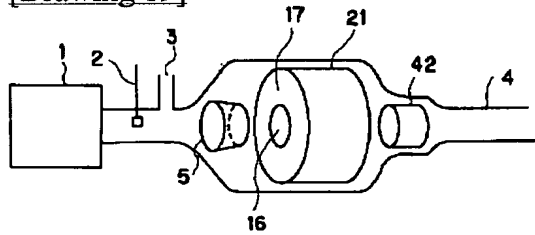
[Drawing 17]



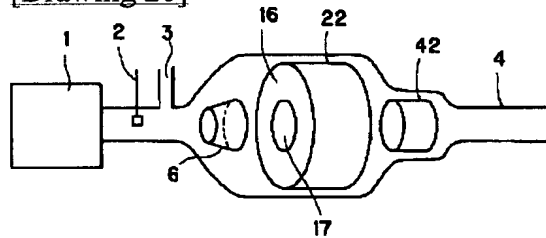
[Drawing 18]



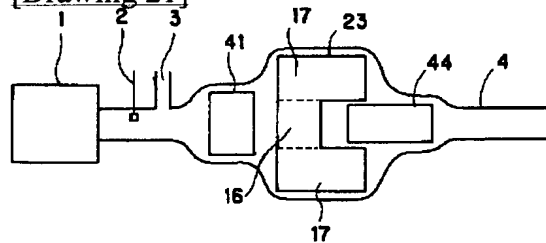
[Drawing 19]



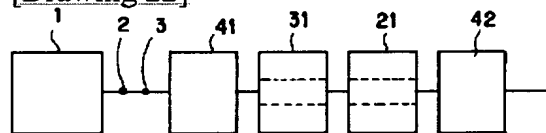
[Drawing 20]



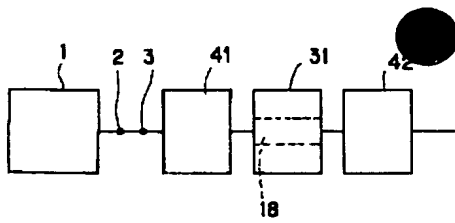
[Drawing 21]



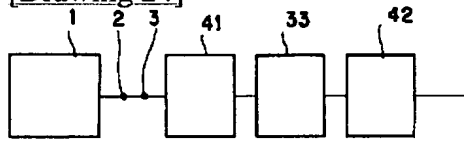
[Drawing 22]



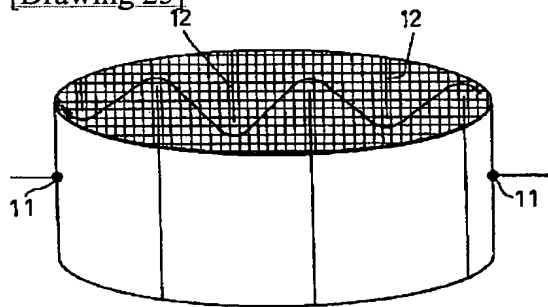
[Drawing 23]



[Drawing 24]



[Drawing 25]



[Translation done.]

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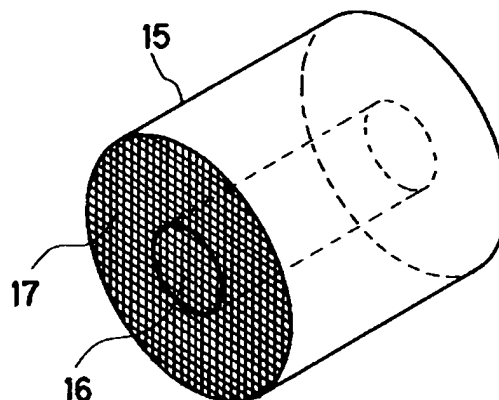
(74)代理人 弁理士 渡邊 一平

(54)【発明の名称】 排ガス浄化用吸着・触媒体、吸着体、排ガス浄化システム及び排ガス浄化方法

(57)【要約】

【構成】 隔壁によって仕切られた、ガス流れ方向に実質的に平行な多数の貫通孔を有するハニカム構造体15上に、炭化水素吸着能を有する吸着層と三元性能又は酸化性能を有する触媒層とが担持されてなる排ガス浄化用吸着・触媒体であって、前記ガス流れ方向と直角方向に、ある断面で吸着層と触媒層とが分離して担持されている排ガス浄化用吸着・触媒体。

【効果】 内燃機関から排出される排ガス中の有害成分、特にコールドスタート時に大量発生するHCを効率よく浄化することができる。



【特許請求の範囲】

【請求項1】 隔壁によって仕切られた、ガス流れ方向に実質的に平行な多数の貫通孔を有するハニカム構造体上に、炭化水素吸着能を有する吸着層と三元性能又は酸化性能を有する触媒層とが担持されてなる排ガス浄化用吸着・触媒体であって、前記ガス流れ方向と直角方向に、ある断面で吸着層と触媒層とが分離して担持されていることを特徴とする排ガス浄化用吸着・触媒体。

【請求項2】 触媒層が担持された部分の断面積がハニカム構造体の断面積の5～80%である請求項1記載の排ガス浄化用吸着・触媒体。

【請求項3】 吸着層が担持された部分の熱容量が、触媒層が担持された部分の熱容量より大である請求項1記載の排ガス浄化用吸着・触媒体。

【請求項4】 触媒層が担持された少なくとも一部分のガス流れ方向に対する長さが、吸着層が担持された部分のガス流れ方向に対する長さより短い請求項1記載の排ガス浄化用吸着・触媒体。

【請求項5】 触媒層が担持された少なくとも一部分の開口率が、吸着層が担持された部分の開口率より大である請求項1記載の排ガス浄化用吸着・触媒体。

【請求項6】 吸着層中に触媒成分が含まれるか、又は吸着層の表面に触媒成分を含む層が被覆担持された請求項1ないし5のいずれかに記載の排ガス浄化用吸着・触媒体。

【請求項7】 吸着層がゼオライトを主成分とする請求項1ないし6のいずれかに記載の排ガス浄化用吸着・触媒体。

【請求項8】 ゼオライトのSi/Alモル比が40以上である請求項7記載の排ガス浄化用吸着・触媒体。

【請求項9】 ゼオライト中に、Pt、Pd、Rhのうちの少なくとも一種の貴金属が含まれる請求項7記載の排ガス浄化用吸着・触媒体。

【請求項10】 ゼオライト中に、周期表のIB族元素(Cu、Ag、Au)のイオンが少なくとも一種含まれる請求項7記載の排ガス浄化用吸着・触媒体。

【請求項11】 ゼオライト中のIB族元素のイオンの含有率が、ゼオライト中のAl原子に対して20%以上である請求項10記載の排ガス浄化用吸着・触媒体。

【請求項12】 ゼオライト中に、更にMg、Ca、Sr、Ba、Y、La、Ti、Ce、Mn、Fe、Cr、Ni、Znの各種イオンから選ばれる少なくとも一種のイオンが含まれた請求項10記載の排ガス浄化用吸着・触媒体。

【請求項13】 触媒層がPt、Pd、Rhのうちの少なくとも一種の貴金属を含む請求項1ないし12のいずれかに記載の排ガス浄化用吸着・触媒体。

【請求項14】 隔壁によって仕切られた、平行な多数の貫通孔を有するハニカム構造体上に炭化水素吸着能を有する吸着層が担持されてなる排ガス浄化用吸着体であ

って、該ハニカム構造体の一部に排ガスが吹き抜ける吹き抜け部が形成されたことを特徴とする排ガス浄化用吸着体。

【請求項15】 吹き抜け部がハニカム構造体の貫通孔と平行に形成された請求項14記載の排ガス浄化用吸着体。

【請求項16】 吹き抜け部がハニカム構造体の貫通孔に対し所定の角度傾かせて形成された請求項14記載の排ガス浄化用吸着体。

【請求項17】 吸着層中に触媒成分が含まれるか、又は吸着層の表面に触媒成分を含む層が被覆担持された請求項14ないし16のいずれかに記載の排ガス浄化用吸着体。

【請求項18】 吸着層がゼオライトを主成分とする請求項14ないし17のいずれかに記載の排ガス浄化用吸着体。

【請求項19】 ゼオライトのSi/Alモル比が40以上である請求項18記載の排ガス浄化用吸着体。

【請求項20】 ゼオライト中に、Pt、Pd、Rhのうちの少なくとも一種の貴金属が含まれる請求項18記載の排ガス浄化用吸着体。

【請求項21】 ゼオライト中に、周期表のIB族元素(Cu、Ag、Au)のイオンが少なくとも一種含まれる請求項18記載の排ガス浄化用吸着体。

【請求項22】 ゼオライト中のIB族元素のイオンの含有率が、ゼオライト中のAl原子に対して20%以上である請求項21記載の排ガス浄化用吸着体。

【請求項23】 ゼオライト中に、更にMg、Ca、Sr、Ba、Y、La、Ti、Ce、Mn、Fe、Cr、Ni、Znの各種イオンから選ばれる少なくとも一種のイオンが含まれた請求項21記載の排ガス浄化用吸着体。

【請求項24】 排気管内に請求項1ないし13のいずれかに記載の吸着・触媒体を少なくとも1つ設置し、更に該吸着・触媒体の排ガス流れ方向下流側に、ハニカム構造体上に触媒層が担持されてなる触媒体を設置してなることを特徴とする排ガス浄化システム。

【請求項25】 更に、吸着・触媒体の排ガス流れ方向上流側にも、ハニカム構造体上に触媒層が担持されてなる触媒体を設置した請求項24記載の排ガス浄化システム。

【請求項26】 更に、吸着・触媒体と触媒体の間に電気通電加熱式ヒーターを設置した請求項24記載の排ガス浄化システム。

【請求項27】 更に、吸着・触媒体と触媒体の間、及び/又は吸着・触媒体の排ガス流れ方向上流側に設置した触媒体の更に上流側に電気通電加熱式ヒーターを設置した請求項25記載の排ガス浄化システム。

【請求項28】 排ガスを偏流させ、吸着・触媒体の触媒層が担持された部分の排ガス流量が、吸着層が担持さ

れた部分の排ガス流量より大きくなるようにした請求項24ないし27のいずれかに記載の排ガス浄化システム。

【請求項29】 更に、吸着・触媒体の排ガス流れ方向下流側に設置された触媒体よりも排ガス流れ方向上流側に、請求項14ないし23のいずれかに記載の吸着体を少なくとも1つ設置した請求項24ないし28のいずれかに記載の排ガス浄化システム。

【請求項30】 排気管内に請求項14ないし23のいずれかに記載の吸着体を少なくとも1つ設置し、更に該吸着体の排ガス流れ方向下流側に、ハニカム構造体上に触媒層が担持されてなる触媒体を設置してなることを特徴とする排ガス浄化システム。

【請求項31】 更に、吸着体の排ガス流れ方向上流側にも、ハニカム構造体上に触媒層が担持されてなる触媒体を設置した請求項30記載の排ガス浄化システム。

【請求項32】 更に、吸着体と触媒体の間に電気通電加熱式ヒーターを設置した請求項30記載の排ガス浄化システム。

【請求項33】 更に、吸着体と触媒体の間、及び／又は吸着体の排ガス流れ方向上流側に設置した触媒体の更に上流側に電気通電加熱式ヒーターを設置した請求項31記載の排ガス浄化システム。

【請求項34】 排ガスを偏流させ、排ガス流の一部が吹き抜け部を通過するようにした請求項30ないし33のいずれかに記載の排ガス浄化システム。

【請求項35】 請求項24ないし34のいずれかに記載の排ガス浄化システムを用い、内燃機関のコールドスタート時に発生する排ガス中の炭化水素等が吸着・触媒体及び／又は吸着体の吸着層に吸着され、該吸着層の排ガスによる温度上昇に伴って該吸着層から脱離していく過程において、ある一定期間排ガス中に酸化性ガスの添加を行うか、又は燃焼用空気と燃料量との調節を行うことにより、酸素過剰の排ガス組成とし、脱離した炭化水素等を吸着・触媒体及び／又は触媒体の触媒層で燃焼せしめることを特徴とする排ガス浄化方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、排ガス中の有害物質、特にコールドスタート時に多量に発生する炭化水素（HC）等を効果的に浄化できる排ガス浄化システム及び排ガス浄化方法に関する。

【0002】

【従来の技術】米国排ガス規制強化に対応するFTP試験（LA-4モード）では、エンジクラク後のコールドスタート時、140秒以内（1山加速以内）に全HCエミッション量の7～8割を放出する。しかし、この間、従来の三元触媒は作用温度に到達するまでかなりの時間がかかるため、大部分のHCは浄化されないまま放出されることになる。

【0003】この問題を解決するために、電気通電加熱方式の触媒（Electrically-Heated Catalyst；以下、「EHC」という）や、ゼオライトを主成分とする吸着材を排ガス管路中に配設する技術が提案されている。例えば、特開平5-31359号公報には、EHC、吸着体、メイン触媒の三要素が順序は任意であるが、排ガス流路に直列に配置された自動車排ガス浄化用触媒コンバーターが開示されている。また、SAE paper No. 920847には、触媒が十分に活性化された段階でHCを脱離させる方法として、吸着材の上流側にバルブを設置するバイパス方式が提案されている

【0004】

【発明が解決しようとする課題】しかしながら、特開平5-31359号公報においては、上記の三要素について、コールドスタート時のエミッション低減のために最適な配置を特に開示しておらず、EHCへの投入電力を低く抑えること等に関しての考慮もなされていない。また、SAE paper No. 920874のようにバイパス方式を採用したものは、浄化能の点では好適に作用するが、システムが複雑となること及び配管中の耐熱バルブの信頼性が乏しくなること等実用上多くの問題がある。

【0005】本発明は、上記のような従来技術の問題点に鑑みてなされたものであり、その目的とするところは、バイパス方式等のように複雑なシステムを要することなく、排ガス中の有害物質、特にコールドスタート時に多量に発生するHC等を効果的に浄化できる排ガス浄化用吸着・触媒体、吸着体、排ガス浄化システム及び排ガス浄化方法を提供することにある。

【0006】

【課題を解決するための手段】本発明によれば、隔壁によって仕切られた、ガス流れ方向に実質的に平行な多数の貫通孔を有するハニカム構造体上に、炭化水素吸着能を有する吸着層と三元性能又は酸化性能を有する触媒層とが担持されてなる排ガス浄化用吸着・触媒体であって、前記ガス流れ方向と直角方向に、ある断面で吸着層と触媒層とが分離して担持されていることを特徴とする排ガス浄化用吸着・触媒体、が提供される。

【0007】また、本発明によれば、隔壁によって仕切られた、平行な多数の貫通孔を有するハニカム構造体上に炭化水素吸着能を有する吸着層が担持されてなる排ガス吸着体であって、該ハニカム構造体の一部に排ガスが吹き抜ける吹き抜け部が形成されたことを特徴とする排ガス浄化用吸着体、が提供される。

【0008】更に、本発明によれば、排気管内に上記のような排ガス浄化用吸着・触媒体を少なくとも1つ設置し、更に該吸着・触媒体の排ガス流れ方向下流側に、ハニカム構造体上に触媒層が担持されてなる触媒体を設置してなることを特徴とする排ガス浄化システム、が提供される。

【0009】更に、本発明によれば、排気管内に上記のような排ガス浄化用吸着体を少なくとも1つ設置し、更に該吸着体の排ガス流れ方向下流側に、ハニカム構造体上に触媒層が担持されてなる触媒体を設置してなることを特徴とする排ガス浄化システム、が提供される。

【0010】更にまた、本発明によれば、上記のような排ガス浄化システムを用い、内燃機関のコールドスタート時に発生する排ガス中の炭化水素等が吸着・触媒体及び／又は吸着体の吸着層に吸着され、該吸着層の排ガスによる温度上昇に伴って該吸着層から脱離していく過程において、ある一定期間排ガス中に酸化性ガスの添加を行うか、又は燃焼用空気と燃料量との調節を行うことにより、酸素過剰の排ガス組成とし、脱離した炭化水素等を吸着・触媒体及び／又は触媒体の触媒層で燃焼せしめることを特徴とする排ガス浄化方法、が提供される。なお、本発明において、ハニカム構造体とは、隔壁によって仕切られた、平行な多数の貫通孔を有する構造体を意味し、板状型等をも含む。

【0011】次に、本発明の基本原理解を説明する。通常、配管内に吸着体と触媒体とが排ガス流れ方向の上流側から順に配設された場合、コールドスタート時に吸着体が排ガスによって加熱され、次いで触媒体が加熱されるため、上流側の吸着体が下流側の触媒体より常に先に温度上昇する。したがって、吸着体の吸着層がHCを好適に吸着し、脱離し始める時(80~100℃位)に、下流側の触媒体はまだ着火温度に到達していない(100℃未満)ので、結果的に脱離したHCは未浄化のまま系外へ流出する。また、仮に吸着体の吸着層に触媒成分が含まれていたとしても、脱離したHCの浄化効率是不充分である。以上の問題に対し、本発明は、特定の吸着・触媒体又は吸着体を用いて下流側の触媒体の昇温速度を増し、上流側の吸着・触媒体又は吸着体から脱離したHCを効率的に浄化せしめるものである。

【0012】基本原理解を特定の吸着・触媒体を例にとって説明すると、HCが最も多量に発生するスタートのアイドリング時は排ガス流量が少なく、吸着・触媒体の入口面に比較的均一に排ガスが流れ込むため、吸着・触媒体の吸着層が担持された部分(以下、「吸着部」という)に多くのHCが吸着される。次に、加速段階では排ガス流量が多くなるが、この場合、好ましくは、吸着・触媒体の触媒層が担持された部分(以下、「触媒部」という)に多くの排ガスが流れるように、配管構造を工夫するか、吸着・触媒体の直前もしくは直後に排ガス流ガイド等を配置する。

【0013】これとは別の手法として、触媒部の少なくとも一部分のガス流れ方向に対する長さを、吸着部のガス流れ方向に対する長さより短くする手法もとれる。また、触媒部の少なくとも一部分の開口率を吸着部の開口率より大きくするといった手法も用いられる。ここで、開口率とは、ハニカム構造体の断面積に対する、隔壁に

よって仕切られた貫通孔の断面積の総和すなわちガス通過面積の割合を意味する。さらには、吸着層の昇温速度を抑える(HCの脱離開始時期を遅らせる)目的で、種々の方法を用いて吸着部の熱容量を触媒部の熱容量より大きくする手法も用いられる。これらの手法により、加速段階においても、吸着・触媒体の吸着部は排ガスによる加熱を受けにくく、あるいはそれ自体昇温しにくい構造を有することになるため、引き続きある一定期間HCを吸着し続け、HCの脱離へ至る。

【0014】一方、吸着・触媒体の触媒部は、前述の手法等により急峻に加熱され、早期に着火して大きな反応熱を生み、これが対流伝熱によって下流側に配設した触媒体を確実に着火に至らしめる。すなわち、吸着・触媒体の吸着部の昇温を極力抑え、触媒部と下流側の触媒体の昇温を極力速めることにより、結果的に吸着部から脱離したHCは、少なくとも下流側に配置した既に着火状態にある触媒体によって浄化される。

【0015】具体的には、吸着部からHCが脱離し始めた時、下流側の触媒体が150℃以上、好ましくは250℃以上の温度に到達しているようにすることが望ましい。また、脱離したHCを浄化するために不足する酸化剤は、二次空気の導入あるいは燃焼用空気と燃料量の調節によって補給される。なお、ハニカム構造体の材料としては、メタル質のものを用いてもよいが、セラミック、特に多孔質のコーージェライトを用いると、熱伝導が悪く、触媒部から吸着部に熱が伝わりにくいため、吸着部の温度が容易に上昇せず、HCの脱離時期をより遅らせることができるので好ましい。

【0016】また、吸着層のみが担持され、一部の排ガスが吹き抜ける構造の吸着体を配するシステムにおいては、排ガスの熱の一部が吸着体を通り抜けて直接吸着体の下流側の触媒体を加熱し、触媒体を早期に着火することができる。本発明においては、以下の吸着・触媒体、吸着体及びシステムが好適に使用される。

【0017】〔吸着・触媒体〕円形断面を持つハニカム構造体において、断面中心よりある半径を持ち、排ガス流れ方向に円柱状に延びた部位に触媒層を担持し、その外周部に吸着層を担持したものが好ましい。また、触媒部の断面積がハニカム構造体の断面積の5~80%であると触媒の早期着火に特に好ましい。ハニカム構造体の断面形状や触媒部の断面形状が円形でない場合でも、触媒部のハニカム構造体に対する断面積比は5~80%の範囲とするのが好ましい。触媒部のハニカム構造体に対する断面積比が5%未満では、触媒部の早期着火による反応熱が小さく、下流側の触媒体の昇温が不充分なものとなり、80%を超えると、吸着部の吸着能が低下する。

【0018】更に、吸着部と触媒部の温度差を大きくするために、吸着部のリブ厚を大きくする、セル密度を高くする、吸着部におけるハニカム構造体材料の気孔率を

小さくする、吸着部の材質をメタルハニカム等の熱容量の大きな材質とする、吸着層の担持量を増やす等により、吸着部の熱容量を触媒部の熱容量より大きくすることが好ましい。なお、触媒部については逆のことが言え、触媒部の熱容量を吸着部のそれより小さくする種々の手法が用いられる。中でも、触媒部のリブ厚を小さくする、セル密度を低くする、触媒層の担持量を減らす等の手法は触媒部の開口率を増大させ、その結果、触媒部の低熱容量化、低圧損化にも寄与するので好ましい。

【0019】また、触媒部の少なくとも一部分の排ガス流れ方向に対する長さを、吸着部の排ガス流れ方向に対する長さより短くすることが好ましく、これにより、触媒部の熱容量が小さくなるとともに、圧損が小さくなるため、エンジン加速時に多くの排ガスが流れ、触媒部が早期に着火する。このように触媒部を短くした状態は、ハニカム構造体の排ガス流れ方向の一部のみに触媒層を担持することでも得られるが、図3の斜視図(a)及び断面図(b)に示すように、ハニカム構造体15の一部をくりぬいて、触媒部16の排ガス流れ方向の一部を空洞化することで、触媒部16の排ガス流れ方向に対する長さを、吸着部17のそれより短くするのが特に好ましい。

【0020】また、触媒部又は吸着部は、どちらか一方が他方を取り囲む状態でもよく、更に触媒部又は吸着部がそれぞれ2箇所以上に分かれていてもよい。また、吸着・触媒体の前端部若しくは後端部又は長さ方向の少なくとも一部の断面の全体あるいは一部が、吸着部あるいは触媒部となっていてよく、吸着部あるいは触媒部が排ガス流れ方向に連続してなくてもよい。

【0021】〔吸着体〕排ガスが吹き抜ける吹き抜け部を形成したハニカム構造体で、吹き抜け部以外の部分には吸着層が担持されており、吹き抜け部はハニカム構造体の一部が排ガス入口から出口まで排ガス流れ方向と平行に何も担持されていないものでもよいが、その部分が空洞となっているものが好ましい。空洞部又は非担持部は2箇所以上でもよい。空洞部又は非担持部の断面積は、ハニカム構造体断面積の50%未満であることが好ましい。また、吹き抜け部は、ハニカム構造体の貫通孔と平行に形成してもよいし、貫通孔に対し所定の角度傾かせて形成し、一部の排ガスはその吹き抜け部を通過し、一部の排ガスが吸着層担持部へ流れ込んで、HCの吸着・脱離が行われる構造としてもよい。

【0022】〔システム〕吸着・触媒体の下流側に吸着部から脱離したHCを浄化するための触媒体を設ける。更に、吸着・触媒体の上流側に早期着火用の触媒体を設けることが好ましく、特に上流側触媒体の反応熱を迅速に吸着・触媒体の触媒部に伝達するよう設計することが好ましい。これらの触媒体はハニカム構造体上に触媒層が担持されたものである。また、吸着・触媒体とその上流側及び／又は下流側に設置した触媒体との間、及び／又は吸着・触媒体の上流側に設置した触媒体の更に上流

側に電気通電加熱式のヒーター又はEHCを設けることで、吸着・触媒体の吸着部のHC脱離コントロール、触媒部の早期着火、及び／又は触媒体の早期着火が可能となり好ましい。また、排気管の形状・構造を工夫するか、ジャマ板や排気流ガイド等の設置により、排ガスを偏流させることで、エンジン加速時に吸着・触媒体の触媒部に吸着部よりも多量の排ガスを流し、触媒部を早期着火させる設計でもよい。

【0023】また、吸着体と吸着・触媒体とを組み合わせ、排ガス流内に連続して設置し、これらが全体として吸着・触媒体の機能を発揮するよう設計することも好ましいシステムである。この場合、これらの吸着体と吸着・触媒体を組み合わせたものの下流側には、吸着体から脱離したHCを浄化するための触媒体が必要であり、更にこれらの上流側にも触媒体が設けられることが好ましい。一方、吸着・触媒体の代わりに吸着体を組み込んだシステムも吸着・触媒体を組み込んだシステムと基本的に同一であり、吸着体の下流側に吸着体から脱離したHCを浄化するための触媒体を設ける。更に、上述した吸着・触媒体を組み込んだシステムと同様に、電気通電加熱式ヒーターを設けたり、排ガスを偏流させて排ガス流の一部が吸着体の吹き抜け部を通過するような構成としたシステムも好適に使用できる。吸着・触媒体や吸着体は、それぞれ複数個設けてもよい。

【0024】更に、FTP試験全体の浄化特性も向上させるため、これら吸着・触媒体及び／又は吸着体を使用したシステムの下流側に、エンジン排気量に対してある程度の容量を持った触媒体を設置することが好ましい。吸着・触媒体及び／又は吸着体を含んだシステムの設置位置としては、触媒層の早期着火のため、エンジン近傍に設置することが好ましい。また、吸着・触媒体及び／又は吸着体とその上流・下流に設置される触媒体との間隔は、上流側の触媒層で発生した反応熱を迅速に下流側の触媒層に伝え、下流側の触媒層の着火を促進させるため、近接していることが好ましい。

【0025】コールドスタート時に発生したHCを好適に低減するためには、少なくとも触媒体又は触媒部が早期着火することが肝要である。通常コールドスタート時に起こり得る燃料リッチ領域では、触媒体又は触媒部による燃焼反応が起こりにくく、加えて反応熱による加熱促進効果も期待できないので、最もエンジンに近い触媒体又は吸着・触媒体の上流側から酸化性のガス（例えば二次空気）を導入するための酸化性ガス導入機構（例えば二次空気導入機構）を設置するか、燃料量と燃焼用空気の量との調節を行うための燃料-燃焼用空気調節機構（A/F調節機構）を設置して、コールドスタート時に酸素過剰へ排ガス組成を調節する必要がある。

【0026】なお、ここでいう酸素過剰の排ガス組成とは、通常の格別な制御手段を有さない内燃機関のコールドスタート時の排ガス組成に対し、酸素過剰側の組成を

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とることを意味する。具体的には、ガソリン車を例にとるならば、空燃比で14.0（弱還元側）以上、好ましくは14.6～19.0（当量点から酸化側）のリーン側にシフトさせる。このようにリーン側にシフトさせることにより、触媒体（又は触媒部）の酸化活性が飛躍的に向上する。なお、改質ガソリンやメタノール等を燃料にする場合には、理論空燃比そのものが変わるので、このような場合には前述の空燃比を当量比入で換算して、同一の値になるよう、好ましくはリーン側にシフトさせる。

【0027】また、吸着部又は吸着体に吸着されたHCが、吸着部又は吸着体から脱離し始めた時、一時的に排ガス組成は還元側にシフトするので、この時、触媒部又は下流側の触媒体が着火温度に到達していても、脱離したHCの燃焼反応が不十分な場合もあり得る。このため、吸着・触媒体又は下流側の触媒体の前方（上流側）に、少なくとも1つの酸化性ガス導入機構及び／又は燃料-燃焼用空気調節機構を設置して、脱離したHCを触媒部又は触媒体で効率よく燃焼させ得る酸素過剰の排ガス組成とすることが必要である。すなわち、触媒部又は触媒体を早期着火するため、及び吸着部又は吸着体から脱離したHCを触媒部又は下流側の触媒体で好適に除去するための2つの目的で、酸化性ガス導入機構及び／又は燃料-燃焼用空気調節機構が必要となる。

【0028】なお、吸着部又は吸着体に吸着されたHCが吸着部又は吸着体から脱離し始めたことを検知可能な検出手段、例えばO₂センサーやHCセンサーを、少なくとも吸着・触媒体又は吸着体と下流側の触媒体との間に設置して、HCの脱離をこの検出手段で検知し、その信号に従って酸化性ガス導入機構あるいは燃料-燃焼用空気調節機構を作動させることが好ましい。触媒部又は触媒体を早期着火させるためには、一般には吸着・触媒体又は触媒体の最前方に搭載されたA/F調節用O₂センサーの信号に従うか、あるいは予めコールドスタート時に起こり得るリッチ領域を回避するための外部プログラムに従って、酸化性ガス導入機構又は燃料-燃焼用空気調節機構を作動させる。酸化性ガス導入機構と燃料-燃焼用空気調節機構を両方併設してもよい。

【0029】また、吸着部又は吸着体から脱離したHCを下流側の触媒体で好適に燃焼させるために、酸化性ガス導入機構は、少なくとも下流側の触媒体の前方（上流側）の任意の位置に1箇所設けるが、前述の最もエンジンに近い触媒体又は吸着・触媒体の触媒部の早期着火のために、その上流側に設ける酸化性ガス導入機構と兼用することができ、また別個に配置してもよい。更に酸化性ガス導入機構を複数個設ける場合は、個別に制御してもよく、また連動させてもよい。

【0030】内燃機関から排出されるHC、CO、NO_x等の有害成分を好適に除去せしめるため、吸着・触媒体の触媒部及び触媒体は、触媒層として、少なくともP

t、Pd、Rhのうちの少なくとも一種の貴金属を含有する耐熱性酸化物が、耐熱性無機質からなるハニカム構造体上に被覆されてなるものであることが好ましい。ハニカム構造体の材質としては、耐熱性、耐熱衝撃性の点から、コーディエライトやフェライト系ステンレスであることが好ましい。

【0031】なお、これらの貴金属は、Al₂O₃、SiO₂、TiO₂、ZrO₂等の耐熱性酸化物及びこれらの複合酸化物に担持して用いられる。特に100m²/g以上の比表面積からなるAl₂O₃を用いると貴金属が高分散に担持され低温着火特性と耐熱性が向上し好ましい。更に、耐熱性酸化物にはCeO₂、La₂O₃、CeO₂-ZrO₂等の酸素貯蔵能がある酸化物を5～30wt%添加すると、定常活性が向上し特に好ましい。触媒部又は触媒体中の貴金属の総担持量は20～130g/ft³が好ましく、またRh担持量は2～30g/ft³の範囲が好ましい。また、Pdのみを40～200g/ft³担持させることで、低温着火が可能となり好ましい。

【0032】吸着部又は吸着体は、前述の耐熱性無機質からなるハニカム構造体上にゼオライトを主成分とする吸着層が被覆されたものであることが好ましい。HC等の有害成分を吸着し得る吸着材としては、ゼオライト、活性炭等があるが、バイパス方式を用いることなく排気系に吸着体を配設するには、少なくとも500℃以上の耐熱性が必要であり、ゼオライトを用いるのが好ましい。ゼオライトは、天然品、合成品のいずれでも良く、また種類は特に限定されないが、耐熱性、耐久性、疎水性の点でSi/Alモル比が40以上のものが好適に用いられる。具体的にはZSM-5、USY、β-ゼオライト、シリカライト、メタロシリケート等が好適に使用できる。

【0033】また、ゼオライトは、一種だけでなく複数種を組み合わせて用いることもできる。例えば、ゼオライトのミクロ孔の大きさが約0.55nmと比較的小さな細孔をもつZSM-5は、プロペン等の小分子の吸着に有利であり、逆にトルエンやキシレンの如く大分子の吸着には不向きである。これに対し、ミクロ孔の大きさが約0.74nmの比較的大きな細孔をもつUSYは、プロペン等の小分子の吸着は不利であり、トルエンやキシレン等の大分子の吸着に有利である。したがって、ZSM-5とUSYを混在させてハニカム構造体に被覆するのも好適な手法の1つである。更に、ガス流れ方向に対してZSM-5とUSYを区分して担持するようにしてもよく、この場合、ZSM-5は150℃の比較的高い温度まで吸着保持できるので上流側に担持することが好ましい。

【0034】なお、ゼオライトは単独でも吸着材として使用できるが、HC等の吸着時に並発するコーキングを制御するためにPt、Pd、Rhのうちの少なくとも一種以上の貴金属を担持するのが好ましく、これによりゼ

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オライトの吸着能が低下することなく再生できる。ゼオライトに担持される貴金属としては、Pdが最も安価で再生能が高く好ましい。また、貴金属の担持方法は、熱的安定性の点でイオン交換法によるのが好ましい。更に、貴金属の担持量は、5～40g/ft³（ハニカム体積）が、コスト及び再生能の点で好ましい。ゼオライトをハニカム構造体に担持する場合、必要に応じて5～20wt%のAl₂O₃やSiO₂の無機バインダーを含ませてもよく、これによりHC等の吸着能をそこなうことなく強固に担持される。

【0035】以上のように、ゼオライトに貴金属を担持させた場合、結果として、貴金属はゼオライトの再生能だけではなく触媒作用も有するが、ゼオライト中の貴金属は凝集し易く、触媒としては耐久性が不十分であるので、ゼオライトからなる吸着層に触媒体で用いる触媒層と同等の触媒成分を含有させる、あるいは、吸着層の表面に触媒成分を含む触媒層を被覆して用いることができる。この場合、吸着部又は吸着体は耐久性のある触媒成分を含むことになるので、コールドスタート以降の定常走行時にも好適に浄化能を示し好ましい。また、触媒成分を添加することは、ゼオライトのコーキングを抑制する効果があるので、ゼオライト中に貴金属を添加する必要は必ずしもない。

【0036】また、ゼオライト中に周期表のIB族元素（Cu、Ag、Au）のイオンを少なくとも一種含ませるのも、ゼオライトのHC吸着能を向上させるので好ましい。この場合、上記イオンの含有率が小さいとHC吸着能向上に対して効果が薄いので、ゼオライトの上記イオンの含有率は、ゼオライト中のAl原子に対して20%以上であることが好ましく、40%以上であるとより好ましい。これらのイオンは先述した貴金属と任意に組み合わせゼオライト中に含ませてもよい。更に、上記IB族元素のイオンに加えて、Mg、Ca、Sr、Ba、Y、La、Ti、Ce、Mn、Fe、Cr、Ni、Znの各種イオンから選ばれる少なくとも一種のイオン、好ましくはMg、Ca、Fe、Crのイオンのうちの少なくとも一種のイオンをゼオライト中に含有させると、耐熱性が向上し望ましい。

【0037】吸着部又は吸着体において、吸着層の表面に触媒層を被覆する好ましい例の1つとして、ハニカム構造体の表層に貴金属が担持されたZSM-5、USY、β-ゼオライト等の高シリカ含有ゼオライトを第1層として被覆し、更にその表面に貴金属が担持されたAl₂O₃-CeO₂複合酸化物を第2層として被覆した層型の吸着・触媒体又は吸着体が挙げられる。このような層型の吸着・触媒体又は吸着体は、第2層の主成分であるAl₂O₃がコールドスタート時の排ガス中に含まれるH₂Oを選択的に吸着するブレイドライヤーの効果もち、第1層が受け持つHC等の吸着を高める。加えて、排気温の上昇とともに表層側の触媒成分を含む第2層か

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ら加熱され、第1層のゼオライト成分が吸着したHC等を脱離する時点で第2層の触媒が好適に作用する。このHC等が脱離する時点で、酸化性ガスの添加、又は燃焼用空気量と燃料量の調節により酸素過剰の排ガス組成としてあることが不可欠であり、これにより第2層の触媒作用が飛躍的に向上する。

【0038】なお、ハニカム構造体に、貴金属が担持された触媒成分と、ゼオライト成分とが層型ではなく混在された状態で担持されていても、比較的良好に作用する。ゼオライト成分と触媒成分の重量比は、50～85：15～50であり、ゼオライト成分を多く含むことが好ましい。ハニカム構造体への担持量は、ゼオライト成分が0.05～0.40g/cc、触媒成分が0.02～0.20g/ccの範囲とするのが好ましい。

【0039】本発明では、排気系中に、触媒部又は触媒体の早期着火を達成する目的で、少なくとも1つの電気通電加熱式ヒーター（Electrical Heater；以下、「EH」という）を配置することも好ましい。EHは、フェライト等の耐熱性金属質からなるハニカム構造体に通電のための電極を設けて構成したものであることが、圧損、耐熱性の点で好ましく、更にこのEH上に少なくとも貴金属を含有する耐熱性無機酸化物からなる触媒層を被覆してEHC（すなわち、電気通電加熱方式の触媒体）として用いると、触媒の反応熱の助けをかりてヒーターの加熱に要する電力を低減できるためより好ましい。

【0040】本発明の排ガス浄化方法において、浄化システム中の触媒部又は触媒体を活性化するためには酸化性のガスを導入すればよく、酸化性のガスとしてはオゾン、O₂⁻、二次空気等を用いることができるが、これらのうちエアポンプ等の簡易な装置で導入可能な二次空気が最も好ましい。酸化性ガスを導入する時期は、吸着・触媒体又は触媒体をエンジン近傍に配置している場合は、排ガスの排気熱による加熱が速いので、エンジン始動時と実質的に同時に導入を開始してもよい。また、導入停止時期は、エンジンの暖機とともにA/F調節用O₂センサーが作動し、当量比で運転されたときが目安となり、ヒーター付O₂センサーの場合はエンジンクランク後から20～50秒、ヒーター無O₂センサーの場合はエンジンクランク後から40～140秒程度経過した時点である。

【0041】一方、吸着部又は吸着体から脱離したHCを触媒部又は下流側の触媒体で効率よく燃焼せしめるために導入する酸化性ガスの導入時期は、吸着・触媒体又は吸着体下流側の検出手段（O₂センサー、HCセンサー等）によって検知するのが好ましい。導入量は、吸着・触媒体又は下流側の触媒体に対し、排ガス組成が酸素過剰になればよく、検出手段からの出力をフィードバックして制御する方法も用いることができる。一般に吸着部又は吸着体の温度が80～100℃を越えた場合にH

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Cは脱離し始めるので、導入開始時期は吸着体の位置にも依存するが、エンジンクランク後から50秒間の間に導入を開始し、導入の停止はエンジンクランク後から40~140秒程度経過した時点である。

【0042】EHやEHCを併用する場合は、酸化性ガスの導入と同時に電圧を印加すると、吸着部より脱離したHCが触媒部やその下流の触媒体などで効率よく浄化され好ましい。酸化性ガスの導入量は、エンジン排気量によっても異なるが、50~300l/min程度とする。必要以上に導入すると、触媒部又は下流の触媒体を冷却することになるので、空燃比が当量点近傍になるように導入するのが最も好ましい。酸化性ガス導入量は一定としても、また適宜可変させてもよい。

【0043】酸化性ガスを導入する方法の他に、エンジンの運転方法、すなわち燃焼用空気量と燃料量とを調節して酸素過剰の排ガス組成を得る方法によっても、同様の効果が得られる。例えば、エンジン点火後、オープンループ制御（O₂センサー使用せず）にて、エアフロセンサー等で検知した空気量に対し、理論燃料より少ない燃料を導入するか、あるいはO₂センサーを用い、予めある一定期間、例えばリーン側へ制御するようコンピューターにて調整するか、さらには、空燃比によりセンサー出力が直線的に変化するPEGOセンサー等を用いて、ある一定期間、例えばリーン側に制御する方法などがある。

【0044】エンジンの点火時は、操作性の点から燃料リッチの状態をとり得るため、これらの方法を用いて排ガス組成を制御できる装置が通常のシステムに加えて必要となる。センサーを用いて排ガス組成を制御する方法は、精度の点で優れるが、センサー自体暖機されるのに時間を要する。これはヒーター付きセンサー等を用いることによりかなりは改善されるものの、エンジンクランク後比較的早く酸素過剰の排ガス組成を得るためには、酸化性ガスを導入するか、センサー以外の制御装置を用いることが好ましい。また、酸化性ガス導入と、燃焼用空気量と燃料量の調節との両方の方法を併用して酸素過剰の排ガス組成を得ることも好適な手法の1つである。

【0045】

【実施例】以下、本発明を実施例に基づいて更に詳細に説明するが、本発明はこれらの実施例に限定されるものではない。

【0046】[吸着・触媒体の作製]：

吸着・触媒体I；直径144mmφ、長さ100mmの日本碍子(株)製コーゼライト質ハニカム構造体（リブ厚150μm、セル密度400セル/平方インチ）の断面の中心点から半径44mm、貫通孔の軸方向長さ100mmの円柱部に γ -Al₂O₃・CeO₂（重量比70：30）を0.23g/cc担持し、次いで、Pd、Pt、Rhを6：5：1の比となるよう80g/ft³担持し、550℃で焼成して触媒層とした。次に、その外周

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部にThe PQ Corporation製のZSM-5（Si/Alモル比=280）を0.15g/cc担持し、550℃で焼成して吸着層とした。以上のようにして、図1に示すように、ハニカム構造体15の断面中央部に触媒層が担持された触媒部16が形成され、その外周部に吸着層が担持された吸着部17が形成された吸着・触媒体Iを得た。

【0047】吸着・触媒体II；上記吸着・触媒体Iと同じハニカム構造体を用い、その断面の中心から半径52mm、貫通孔の軸方向長さ100mmの円柱部に、吸着・触媒体Iと同様にZSM-5を担持、焼成し、その外周部に、吸着・触媒体Iと同様に触媒層を担持、焼成した。以上のようにして、図2に示すように、ハニカム構造体15の断面中央部に吸着層が担持された吸着部17が形成され、その外周部に触媒層が担持された触媒部16が形成された吸着・触媒体IIを得た。

【0048】吸着・触媒体III；上記吸着・触媒体Iと同じハニカム構造体の断面の中心から半径44mm、貫通孔の軸方向長さ50mmの部分を取りぬき、吸着・触媒体用担体とした。次に、 γ -Al₂O₃・CeO₂（重量比70：30）にPd(NO₃)₃水溶液を用いてPdを含浸し、乾燥後550℃で焼成してPd担持 γ -Al₂O₃・CeO₂複合酸化物を得た。この複合酸化物を上記吸着・触媒体用担体の断面の中心から半径44mm、貫通孔の軸方向長さ50mmの部分（くりぬいた部分から貫通孔軸方向に延長した部分）に0.1g/cc担持し、550℃で焼成して触媒層とした。触媒層のPd担持量は150g/ft³となった。次に、ZSM-5に(NH₃)₂Pt(NO₂)₂を用いて90℃で4時間処理してPtをイオン交換し、乾燥後550℃で焼成してPt-イオン交換ゼオライト粉末を得た。この粉末を上記触媒層を担持した部分の外周部に担持し、550℃で焼成し、第1層とした。第1層の担持量は0.15g/cc、Pt量は33.3g/ft³となった。次に、同様に γ -Al₂O₃にRhをブレードした粉末を第1層の上に担持、焼成し、第2層とした。第2層の担持量は0.05g/cc、Rh量は6.7g/ft³となった。更に、 γ -Al₂O₃にPdをブレードした粉末を第2層の上に担持、焼成し、第3層とした。第3層の担持量は0.03g/cc、Pd量は40g/ft³となった。以上のようにして、図3(a)の斜視図及び(b)の断面図に示すように、くりぬかれて貫通孔の軸方向の長さ（排ガス流れ方向の長さ）が外周部に比して短くなったハニカム構造体15の断面中央部に触媒層が担持された触媒部16が形成され、その外周部に触媒成分をも含んだ複層構造の吸着層が担持された吸着部17が形成された吸着・触媒体IIIを得た。

【0049】吸着・触媒体IV；上記吸着・触媒体Iと同じハニカム構造体の断面の中心から半径40mmの円周上を4等分する4つの点をそれぞれ中心とした半径25mm、貫通孔の軸方向長さ100mmの円柱部4箇所に吸着・触媒体Iと同様に触媒層を担持、焼成し、残

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りの部分にZSM-5を担持、焼成した。以上のようにして、図4に示すように、ハニカム構造体15に触媒層が担持された触媒部16が複数形成され、その他の部分に吸着層が担持された吸着部17が形成された吸着・触媒体IVを得た。

【0050】吸着・触媒体V；上記吸着・触媒体Iと同じハニカム構造体を用い、その断面の直径方向に延びる直線を64mmと80mmに区分する直交線を境界として、ハニカム構造体を小断面積部と大断面積部に2分したうちの、小断面積部には吸着・触媒体Iと同様にして触媒層を担持、焼成し、大断面積部には、吸着・触媒体Iと同様にしてZSM-5を担持、焼成した。以上のようにして、図5に示すように、ハニカム構造体15の断面を2分する境界の一方の側に触媒層が担持された触媒部16が形成され、もう一方の側に吸着層が担持された吸着部17が形成された吸着・触媒体Vを得た。

【0051】吸着・触媒体VI；上記吸着・触媒体Iと同じハニカム構造体を用い、その断面の中心を通る直線で4等分される4つの部分のうちの中心点で接触し対向する2つの部分に、吸着・触媒体Iと同様にして触媒層を担持、焼成し、残りの2つの部分に、吸着・触媒体Iと同様にしてZSM-5を担持、焼成した。以上のようにして、図6に示すように、ハニカム構造体15の断面の中心を通る直線で4等分される4つの部分のうちの中心点で接触し対向する2つの部分に、触媒層が担持された触媒部16が形成され、残りの2つの部分に吸着層が担持された吸着部17が形成された吸着・触媒体VIを得た。

【0052】吸着・触媒体VII；外径144mmφ、内径45mmφ、長さ100mmの中空円筒状のコーゼライト質ハニカム構造体（リブ厚300μm、セル密度300セル/平方インチ）と外径44mmφ、長さ100mmの円柱状のコーゼライト質ハニカム構造体（リブ厚100μm、セル密度400セル/平方インチ）を低膨張セラミック接合材で接合し、吸着・触媒体用担体とした。当担体の外周部を構成する300セル/平方インチのハニカム構造体に、吸着・触媒体Iと同様にして触媒層を担持、焼成し、中央部を構成する400セル/平方インチのハニカム構造体に、吸着・触媒体Iと同様にしてZSM-5を担持、焼成した。以上のようにして、図7に示すように、ハニカム構造体15の断面中央部のセル密度が高い部分に、吸着層が担持された吸着部17が形成され、その外周部のセル密度が低い部分に、触媒層が担持された触媒部16が形成された吸着・触媒体VIIを得た。

【0053】[吸着体の作製]：

吸着体I；直径144mmφ、長さ100mmの日本碍子(株)製コーゼライト質ハニカム構造体（リブ厚150μm、セル密度400セル/平方インチ）の断面の中心点から半径44mm、貫通孔の軸方向長さ100mm

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の部分を作りぬいて、吸着体用担体とし、吸着・触媒体Iと同様にして、ZSM-5担持、焼成した。以上のようにして、図8に示すように、ハニカム構造体15の断面中央部に吹き抜け部18が形成された吸着体Iを得た。すなわち、吸着体Iは吸着・触媒体Iの触媒部を吹き抜け部としたものである。

【0054】吸着体II；上記吸着・触媒体Iと同じハニカム構造体の断面の中心から半径40mmの円周上を4等分する4つの点をそれぞれ中心とした半径25mm、貫通孔の軸方向長さ100mmの4つの部分を作りぬいて、吸着体用担体とし、吸着・触媒体Iと同様にしてZSM-5を担持、焼成した。以上のようにして、図9に示すように、ハニカム構造体15に吹き抜け部18が複数形成された吸着体IIを得た。すなわち、吸着体IIは吸着・触媒体IVの触媒部を吹き抜け部としたものである。

【0055】吸着体III；一辺が100mmである立方体形状のコーゼライト質ハニカム構造体に、貫通孔の軸方向と垂直方向に貫通する断面が50mm×20mmのくりぬきを20mmの間隔で2箇所設けて、吸着体用担体とし、吸着・触媒体Iと同様にしてSM-5を担持、焼成した。以上のようにして、図10に示すように、ハニカム構造体15に、貫通孔の軸方向と垂直方向に貫通する吹き抜け部18が形成された吸着体IIIを得た。

【0056】[触媒体の作製]：

触媒体I、II、III、IV；直径93mmφ、長さ33mm（触媒体I）、直径φ99mmφ、長さ99mm（触媒体II）、直径φ144mmφ、長さ100mm（触媒体III）、及び直径φ76mmφ、長さ88mm（触媒体IV）の4種類の日本碍子(株)製コーゼライト質ハニカム構造体（リブ厚150μm、貫通孔数400セル/平方インチ）に γ -Al₂O₃・CeO₂（重量比70：30）を0.23g/cc担持し、次いで、Pd、Pt、Rhを6：5：1の比となるよう80g/ft³担持し、550℃で焼成して、触媒体I、II、III、IVを得た。

【0057】[電気通電加熱式ヒーターの調製]：平均粒径44μm以下のFe粉末、Cr-30Al粉末（重量%）、Fe-50Al粉末（重量%）、Fe-20B粉末（重量%）及びY₂O₃粉末をFe-18Cr-8Al-0.05B-0.5Y₂O₃という組成になるように添加、混合した。この混合物100gあたり、メチルセルロース4gを有機バインダーとして、また、オレイン酸1gを酸化防止剤として添加し、混合した。このように坯土を調製した後、円柱形状のハニカム成形体を押出成形し、得られたハニカム成形体を大気中、90℃で16時間乾燥し、次いで、水素雰囲気下で1325℃に2時間保持して焼結した。更に、空気中1150℃で30分間熱処理を行ってハニカム構造体を得た。得られたハニカム構造体の多孔度は3%であった。

【0058】上記方法により得られた外径93mmφ、

厚さ25mm、隔壁厚さ0.1mm、六角セルよりなるセル密度450セル/平方インチのハニカム構造体に対して、バンドソーを用いた研削加工により、図25に示すようにスリット12を貫通孔の軸と平行な方向に6箇所、スリット間のセル数が7個となるようにして形成し、ヒーターの抵抗が50mΩになるよう調節した。次いで、ヒーター上に、触媒体Iと同一の触媒層を被覆し、電極11をヒーターに配設し、SUS製の缶体内に該缶体と絶縁をとりながら収納した。ヒーターの有効体積は0.131であった。

【0059】[排ガス浄化システムの構成]: 上記により得られた吸着・触媒体、吸着体、触媒体及び電気通電加熱式ヒーターを用いて以下に示すような排ガス浄化システムを構成した。なお、吸着・触媒体、吸着体及び触媒体の種類を示すローマ数字と図中の参照符号との区別を明確にするため、以下のシステムの説明において、図中の参照符号は括弧()を付して記述した。

【0060】システムA: 図11に示すように、エンジン(1)からの排ガス流路の上流側に吸着・触媒体I(21)を、その下流側に触媒体II(42)を設置した。また、エンジン(1)と吸着・触媒体I(21)の間には、上流側にA/F調節用のO₂センサー(2)を、そして下流側に着火促進用の二次空気導入孔(3)を設置した。エンジンマニホールド出口より吸着・触媒体I(21)までの距離は600mm、吸着・触媒体I(21)と触媒体II(42)との間隔は30mmとした。更に、エンジンマニホールド出口より1200mmの位置に触媒体III(図示せず)を設置した。

【0061】システムB: 図12に示すように、エンジン(1)からの排ガス流路に、エンジン(1)側から触媒体I(41)、吸着・触媒体III(23)、触媒体II(42)の順に設置し、また、エンジン(1)と触媒体I(41)の間には、上流側にA/F調節用のO₂センサー(2)を、そして下流側に着火促進用の二次空気導入孔(3)を設置した。エンジンマニホールド出口より触媒体I(41)までの距離は600mm、触媒体I(41)、吸着・触媒体II(23)、触媒体II(42)の各間隔は30mmとした。更に、エンジンマニホールド出口より1200mmの位置に触媒体III(図示せず)を設置した。

【0062】システムC: 図13に示すように、エンジン(1)からの排ガス流路に、エンジン(1)側から、吸着・触媒体III(23)、電気通電加熱式ヒーター(50)、触媒体II(42)の順に設置し、また、エンジン(1)と吸着・触媒体III(23)の間には、上流側にA/F調節用のO₂センサー(2)を、そして下流側に着火促進用の二次空気導入孔(3)を設置した。エンジンマニホールド出口より吸着・触媒体III(23)までの距離は600mm、吸着・触媒体III(23)、電気通電加熱式ヒーター(50)、触媒体II(42)の各間隔は30mmとした。更に、エンジンマニホールド出口より1200mmの位置

に触媒体III(図示せず)を設置した。

【0063】システムD: 図14に示すように、二次空気導入孔(3)と吸着・触媒体III(23)の間に、更に触媒体I(41)を設置した以外は、上記システムCと同様の構成とした。ただし、エンジンマニホールド出口より触媒体I(41)までの距離を600mmとし、触媒体I(41)と吸着・触媒体III(23)の間隔を30mmとした。

【0064】システムE: 図15に示すように、触媒体I(41)と吸着・触媒体III(23)の間に、更にもう1つの電気通電加熱式ヒーター(50')を配置した以外は上記システムDと同様の構成とした。なお、触媒体I(41)、電気通電加熱式ヒーター(50')、吸着・触媒体III(23)の各間隔は30mmとした。

【0065】システムF: 図16に示すように、エンジン(1)からの排ガス流路の上流側に触媒体I(41)を設置し、その下流側に吸着・触媒体I' (21')及び吸着・触媒体I'' (21'')を隣接して設置した。更にその下流側に触媒体II(42)を設置した。また、エンジン(1)と触媒体I(41)の間には、上流側にA/F調節用のO₂センサー(2)を、そして下流側に着火促進用の二次空気導入孔(3)を設置した。エンジンマニホールド出口より触媒体I(41)までの距離は600mm、触媒体I(41)、吸着・触媒体I' (21')、吸着・触媒体I'' (21'')、触媒体II(42)の各間隔は30mmとした。更に、エンジンマニホールド出口より1200mmの位置に触媒体III(図示せず)を設置した。

【0066】システムG: 図17に示すように、エンジン(1)からの排ガス流路に、上流側から触媒体I(41)、吸着・触媒体V(25)、触媒体II(42)の順に設置した。排気管(4)は内径50mmであるが、触媒体I(41)、吸着・触媒体V(25)、触媒体II(42)の各設置部では下方に径が拡大されるように設計した。吸着・触媒体V(25)は上部が触媒部(16)、下部が吸着部(17)となるように設置した。また、エンジン(1)と触媒体I(41)の間には、上流側にA/F調節用のO₂センサー(2)を、そして下流側に着火促進用の二次空気導入孔(3)を設置した。エンジンマニホールド出口より触媒体I(41)までの距離は600mm、触媒体I(41)、吸着・触媒体V(25)、触媒体II(42)の各間隔は30mmとした。更に、エンジンマニホールド出口より1200mmの位置に触媒体III(図示せず)を設置した。

【0067】システムH: 図18に示すように、エンジン(1)からの排ガス流路に、上流側から触媒体I(41)、吸着・触媒体III(23)、触媒体II(42)の順に設置した。排気管(4)の内径は吸着・触媒体III(23)の前後で急激に絞込まれており、吸着・触媒体III(23)の外周部に形成された吸着部(17)の両端面と排気

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管(4)の内壁との間隔は10mmで、吸着部(17)には中央部に形成された触媒部(16)に比して、排ガスが流れにくくなっている。また、エンジン(1)と触媒体I(41)の間には、上流側にA/F調節用のO₂センサー(2)を、そして下流側に着火促進用の二次空気導入孔(3)を設置した。エンジンマニホールド出口より触媒体I(41)までの距離は600mm、触媒体I(41)、吸着・触媒体III(23)、触媒体II(42)の各間隔は30mmとした。更に、エンジンマニホールド出口より1200mmの位置に触媒体III(図示せず)を設置した。

【0068】システムI; 図19に示すように、エンジン(1)からの排ガス流路に、上流側から吸着・触媒体I(21)、触媒体II(42)の順に設置した。排気管(4)の内部には、吸着・触媒体I(21)の前方(上流側)に、排ガスを吸着・触媒体I(21)の中央部に形成された触媒部(16)に較り、触媒部(16)の排ガス流量が外周部に形成された吸着部(17)に比して多くなるようにするための排気流ガイド(5)を設けた。また、エンジン(1)と吸着・触媒体I(21)の間には、上流側にA/F調節用のO₂センサー(2)を、そして下流側に着火促進用の二次空気導入孔(3)を設置した。エンジンマニホールド出口より吸着・触媒体I(21)までの距離は600mm、吸着・触媒体I(21)と触媒体II(42)の間隔は30mmとした。更に、エンジンマニホールド出口より1200mmの位置に触媒体III(図示せず)を設置した。

【0069】システムJ; 図20に示すように、上記システムIの吸着・触媒体Iの代わりに吸着・触媒体II(22)を設置し、排気管(4)の内部には、吸着・触媒体II(22)の前方(上流側)に、排ガスを吸着・触媒体II(22)の外周部に形成された触媒部(16)に流れやすくし、触媒部(16)の排ガス流量が中央部に形成された吸着部(17)に比して多くなるようにするための排気流ガイド(6)を設けた。その他の構成は上記システムIと同様である。

【0070】システムK; 図21に示すように、エンジン(1)からの排ガス流路に、上流側から触媒体I(41)、吸着・触媒体III(23)、触媒体IV(44)の順に設置した。吸着・触媒体III(23)は、断面中央部の触媒部(16)から排ガス流れ方向に延長した部分に形成された、くりかたれた空洞部を有する側の端面が下流側となるように配置し、その空洞部に触媒体IV(44)が、20mm挿入された状態で配置した。排気管(4)は吸着・触媒体III(23)の吸着部(17)から脱離したHCが全て一旦逆方向へ流れてから触媒体IV(44)を通過するよう設計した。また、エンジン(1)と触媒体I(41)の間には、上流側にA/F調節用のO₂センサー(2)を、そして下流側に着火促進用の二次空気導入孔(3)を設置した。エンジンマニホールド出口より触媒体I(41)までの距離は600mm、触媒体I(41)、吸着・触媒体II

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I(23)、触媒体IV(44)の各間隔は30mmとした。更に、エンジンマニホールド出口より1200mmの位置に触媒体III(図示せず)を設置した。

【0071】システムL; 図22に示すように、エンジン(1)からの排ガス流路に、上流側から触媒体I(41)、吸着体I(31)、吸着・触媒体I(21)、触媒体I(42)の順に設置した。また、エンジン(1)と触媒体I(41)の間には、上流側にA/F調節用のO₂センサー(2)を、そして下流側に着火促進用の二次空気導入孔(3)を設置した。エンジンマニホールド出口より触媒体I(41)までの距離は600mm、触媒体I(41)、吸着体I(31)、吸着・触媒体I(21)、触媒体II(42)の各間隔は30mmとした。更に、エンジンマニホールド出口より1200mmの位置に触媒体III(図示せず)を設置した。

【0072】システムM; 図23に示すように、上記システムBの吸着・触媒体IIIの代わりに、断面中央部に吹き抜け部(18)が形成された吸着体I(31)を設置した。その他の構成は上記システムBと同様である。

【0073】システムN; 図24に示すように、上記システムBの吸着・触媒体IIIの代わりに、ハニカム構造体の貫通孔の軸方向と垂直方向に貫通する吹き抜け部が形成された吸着体III(33)を設置した。なお、吸着体III(33)は排ガス流れ方向と吹き抜け部の軸方向が平行となるように排気管内に設置し、かつ吹き抜け部から貫通孔へ排ガスの一部が流出するよう貫通孔端面は開放した。その他の構成は上記システムBと同様である。

【0074】[排ガス浄化システムの評価]; 上記システムA～Nの排ガス浄化性能を評価すべく、排気量2000cc、4気筒エンジン搭載の試験車を使用して、FTP試験(LA-4モード)を実施した。なお、酸素過剰の排ガスを得るために簡易的に二次空気をエアポンプで各々の導入孔からエンジンクランクより90秒間、100l/minで導入した。また、電気通電加熱式ヒーターを構成に含むシステムの場合、電気通電加熱式ヒーターへの電力の投入は12Vバッテリーを用いて行い、エンジンクランク後30秒後から30秒間2kWで通電した。排ガスはCVS法により採取し、エミッション値を算出した。試験結果を表1に示す。

【0075】

【表1】

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システム	HCエミッション	
	B a g 1 A (g)	トータル (g/mile)
A	0.88	0.064
B	0.51	0.042
C	0.86	0.033
D	0.35	0.030
E	0.33	0.028
F	0.85	0.057
G	0.79	0.053
H	0.48	0.040
I	0.92	0.066
J	0.93	0.070
K	0.54	0.045
L	0.50	0.044
M	0.65	0.048
N	0.71	0.051

【0076】〔温度分布の測定〕：上記システムCのFTP試験時に、K熱電対を、吸着・触媒体IIIの触媒部の入口端面より10mm内側の位置（位置A）、吸着部の出口端面より10mm内側の位置（位置B）及び触媒体IIの入口端面より10mm内側の位置（位置C）にそれぞれセットし、FTPスタート時の温度分布（位置Aが、100℃、200℃、300℃に到達した時の位置B及び位置Cの温度）を測定した。その結果を表2に示す。この結果より前方（上流側）に位置する吸着・触媒体IIIの吸着部出口の方が、後方（下流側）に位置する触媒体IIの入口より温度が低いことがわかる。

【0077】

【表2】

位置 A	位置 B	位置 C
100℃	58℃	72℃
200℃	76℃	125℃
300℃	94℃	206℃

【0078】

【発明の効果】以上説明したように、本発明によれば、内燃機関から排出される排ガス中の有害成分、特にコールドスタート時に大量発生するHCを効率よく浄化することができる。

【図面の簡単な説明】

【図1】本発明に係る吸着・触媒体の一実施例を示す説明図である。

【図2】本発明に係る吸着・触媒体の一実施例を示す説明図である。

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【図3】本発明に係る吸着・触媒体の一実施例を示す説明図である。

【図4】本発明に係る吸着・触媒体の一実施例を示す説明図である。

【図5】本発明に係る吸着・触媒体の一実施例を示す説明図である。

【図6】本発明に係る吸着・触媒体の一実施例を示す説明図である。

10 【図7】本発明に係る吸着・触媒体の一実施例を示す説明図である。

【図8】本発明に係る吸着体の一実施例を示す説明図である。

【図9】本発明に係る吸着体の一実施例を示す説明図である。

【図10】本発明に係る吸着体の一実施例を示す説明図である。

【図11】本発明に係る排ガス浄化システムの一実施例を示す説明図である。

20 【図12】本発明に係る排ガス浄化システムの一実施例を示す説明図である。

【図13】本発明に係る排ガス浄化システムの一実施例を示す説明図である。

【図14】本発明に係る排ガス浄化システムの一実施例を示す説明図である。

【図15】本発明に係る排ガス浄化システムの一実施例を示す説明図である。

【図16】本発明に係る排ガス浄化システムの一実施例を示す説明図である。

30 【図17】本発明に係る排ガス浄化システムの一実施例を示す説明図である。

【図18】本発明に係る排ガス浄化システムの一実施例を示す説明図である。

【図19】本発明に係る排ガス浄化システムの一実施例を示す説明図である。

【図20】本発明に係る排ガス浄化システムの一実施例を示す説明図である。

【図21】本発明に係る排ガス浄化システムの一実施例を示す説明図である。

40 【図22】本発明に係る排ガス浄化システムの一実施例を示す説明図である。

【図23】本発明に係る排ガス浄化システムの一実施例を示す説明図である。

【図24】本発明に係る排ガス浄化システムの一実施例を示す説明図である。

【図25】電気通電加熱式ヒーターの一例を示す説明図である。

【符号の説明】

1…エンジン、2…O₂センサー、3…二次空気導入

孔、4…排気管、5…排気流ガイド、6…排気流ガイド

50 ド、11…電極、12…スリット、15…ハニカム構造

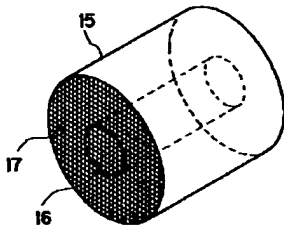
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体、16…触媒部、17…吸着部、18…吹き抜け部、
21…吸着・触媒体I、21'…吸着・触媒体I'、2
1''…吸着・触媒体I''、22…吸着・触媒体II、23
…吸着・触媒体III、25…吸着・触媒体V、31…吸

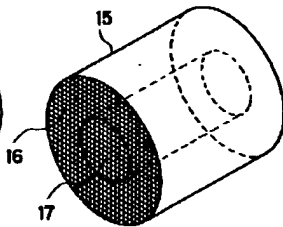
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着体I、33…吸着体III、41…触媒体I、42…触
媒体II、44…触媒体IV、50、50'…電気通電加熱
式ヒーター

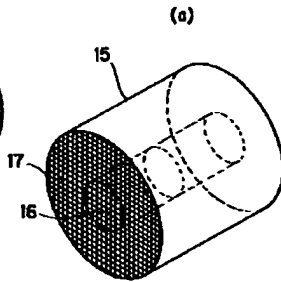
【図1】



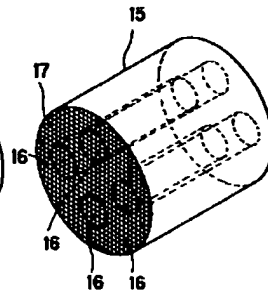
【図2】



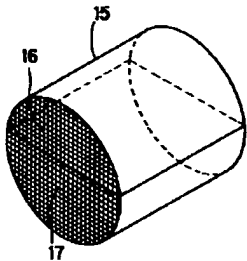
【図3】



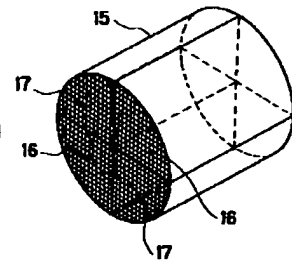
【図4】



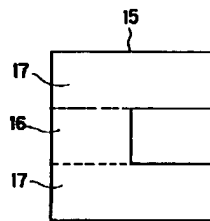
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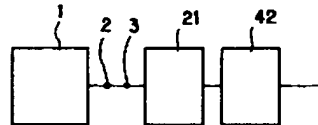
【図6】



(b)

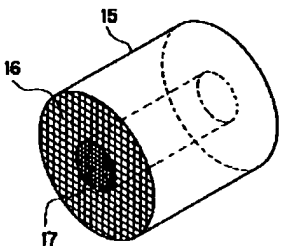


【図11】

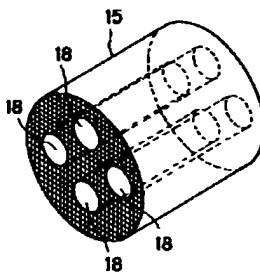


【図8】

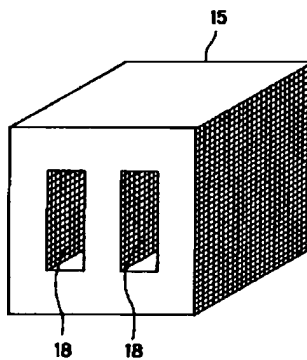
【図7】



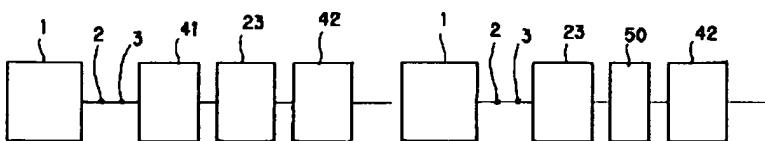
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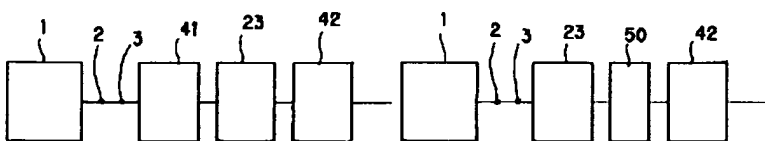
【図10】



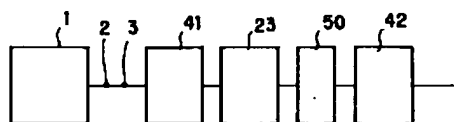
【図12】



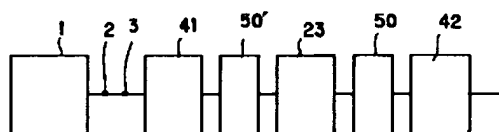
【図13】



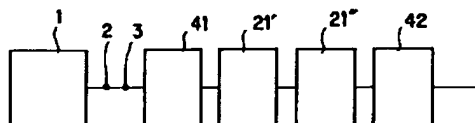
【図14】



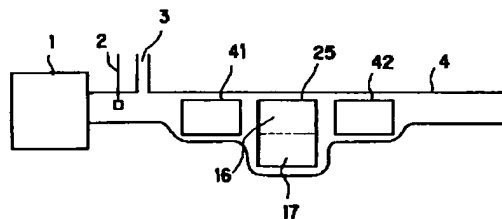
【図15】



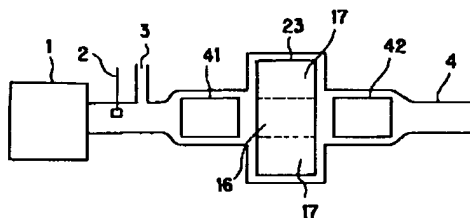
【図16】



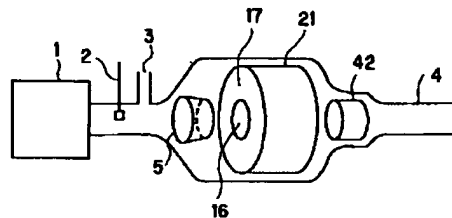
【図17】



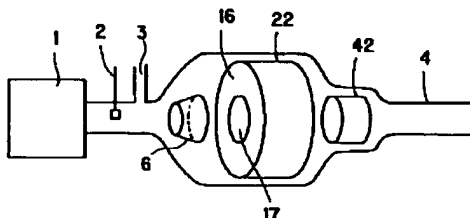
【図18】



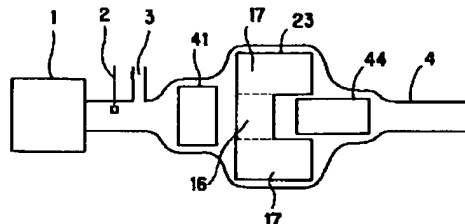
【図19】



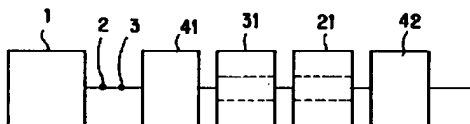
【図20】



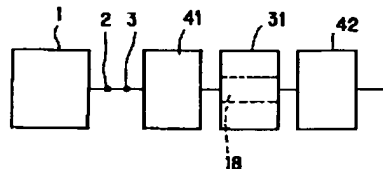
【図21】



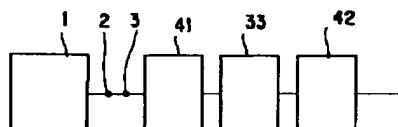
【図22】



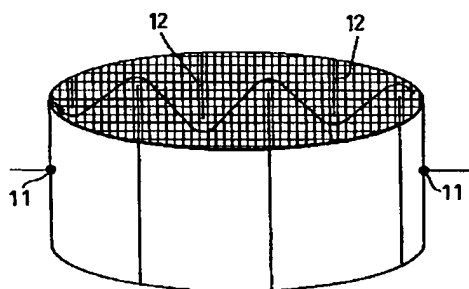
【図23】



【図24】



【図25】



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3/24	Z A B	E		
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